

(57) A novel class of interpretable interpenetrating polymer networks which are dispersible in conventional coating solvents is disclosed. Such dispersions are useful in preparing protective and/or decorative film coatings and are particulary useful in imaging formulations such as photoreists, solder masks and the like. These polymer networks are compounded of at least two interpretable crosslinked polymers. At least one of the polymer networks is formed by polymerization in a solvent. In one embodiment of this invention, at least one polymer network is prepared from macromers to produce a polymer system having functionalized branched or graft linear segments. The solvent dispersible interpenetrating networks of this invention are particularly useful as binders in addition polymerizable compositions containing monomers such as solder masks. Upon exposure to actinic radiation and suitable thermal curing, solder mask coatings of such photoresistive compositions form multiple, e.g., triple, interpretable polymer networks having superior toughness and flexibility.

(56) Solvent dispersible interpretable polymer networks.

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group. European Patent Publication No. 280,979 discloses the use of such a polymer as a binding agent in 45 group. European Patent Publication No. 280,979 discloses the use of such a polymer as a binding agent in the end that can further polymerize, such as an ethylenic, an epoxy, a dicarboxylic acid, a diol or a diamine polymers of molecular weight ranging from several hundred to tens of thousands, with a functional group at 50 the end that can further polymerize, such as an ethylenic, an epoxy, a dicarboxylic acid, a diol or a diamine polymer. Such polymers are defined by Kawakami in the "Encyclopedia of Polymer Science And Engineering", Vol. 9, pp. 195-204 (John Wiley & Sons, New York, 1987) to be conventional monomer with a macromer. Macromers are defined by Kawakami in the "Encyclopedia of 55 Polymer Science And Engineering", Vol. 9, pp. 195-204 (John Wiley & Sons, New York, 1987) to be linear polymers with polymeric arms known and typically are prepared by copolymerizing a core/shell microgels, the shell typically is grafted to the core network by covalent chemical bonding.

Linear polymers with polymeric arms known and typically are prepared by copolymerizing a core/shell microgels, the shell typically is grafted to the core network by covalent chemical bonding. 60 different interior and exterior compositions. Unlike interpenetrating polymer networks, during preparation of that the polymer components can be varied during polymerization to produce core and shell microgels swelling in strong solvent without destroying the crosslinked structure. U.S. Patent 4,726,877 also discloses prepared by emulsion polymerization. Crosslinking renders these microgels insoluble but capable of molecular weight such as of the order of 10⁹ to 10¹⁰ with a particle size of 0.05 to 1 micron in diameter term originated in the paint industry and it includes crosslinked spherical polymer molecules of high 65 compositions, particularly in photopolymerizable resists, is disclosed in U.S. Patent 4,726,877. Microgel is a organic solvent swellable polymer networks, i.e., microgels, are known and their use in photoresistive the exposed area.

Organic solvent swellable polymer networks, i.e., microgels, are known and their use in photoresistive which at least some of the polymeric binding agent is entrapped thereby photobraining or insolubilizing imaging exposure, the monomeric components and crosslinks to form a polymer network in 40 wherein there is no covalent chemical bonding between the different species of polymer chains. During quenched by the binding agent is a simple polymer blend, i.e., an intimate mixture of two or more polymers polymericizable monomeric components having two or more sites of terminal ethylenic unsaturation. Free-radical polymer systems typically have one or more linear polymers as a binding agent and at least one addition Sturge, V. Walworth & A. Shupp, Van Nostrand Reinhold, New York, 1989. Such photopolymerizable disclosed in Chapter 7 of "Imaging Processes and Materials-Resists", Eighth Edition, Edited by J. M. This type of polymer system is considered to be formed in cured photopolymerizable systems such as one is crosslinked and at least one other is linear is designated a semi-interpenetrating polymer network. A polymer system comprising two or more constituents polymers in intimate contact, wherein at least be designated a sequential interpenetrating network.

network, if on the other hand, the synthesis and/or crosslinking are carried out separately, the system may of the constituents is concurrent, the system may be designed a simultaneous interpenetrating "interpenetrating phases" and/or "interpenetrating networks". If the synthesis or crosslinking of two or more limit actual molecular interpenetration. Thus the material sometimes may be described as having catenated, i.e., physically interlocked, and may also be subsequently linked together to a limited extent. While the above definition describes an ideal structure, it is recognized that phase separation may has dimensions comparable with those of the macroscopic material. The constituents networks may be structure in which most chains are crosslinked at least twice to other chains so that the network structure are broken. Each constituent polymer is characterized as an extensive three-dimensional polymer are compacted two or more network polymers that interpenetrate each other to some extent and which are not chemically bound but which are con-catenated such that they can not be separated unless chemical bonds public relations as a polymer system comprising two or more constituents polymer networks that are polymerized and/or crosslinked in the immediate presence of one another. In effect, such a polymer system P. Srigwatt, Pergramon Press, Elmsford, NY, 1989. Interpenetrating polymer networks defined in such Polymer Science", Volume 6, "Polymer Reactions", Edited by G. C. Eastmond, A. Ledwith, S. Russo, and Paul and L. H. Sperry, ACS Books, Washington, DC, 1986, and in pages 423-436 of "Comprehensive 1981, in pages 21-56 of "Multicomponent Polymer Networks and Related Materials", Plenum Press, New York, L. H. Sperry in "Interpenetrating Polymer Networks and Related Materials", Plenum Press, New York, 1981, in pages 21-56 of "Multicomponent Polymer Networks and Related Materials", ACS Adv. in Chem. No. 211, Edited by D. R. 10 product development. Such interpenetrating polymer networks and developments are described by interpenetrating polymer network (also known as IPN) systems are finding increasing uses in polymer such polymer products and including the use of such compositions as photoresists and solder masks.

The present invention is directed to a novel composition of matter which is a type of interpenetrating polymer network. The present invention also relates to liquid and solid imaging compositions containing

BACKGROUND OF THE INVENTION

This application is a continuation in part of U.S. Serial No. 07/414,417, filed September 29, 1989 which is a continuation-in-part of 07/162,966, filed March 2, 1988, now abandoned.

CROSS REFERENCE TO RELATED APPLICATIONS

solvent, such as organic solvent. Dispersible is used in its conventional sense; the term excludes a latex. A further criterion which is necessary for the two polymer networks is an ability to be dispersible in a chains of the individual networks.

to be catenated, i.e., a physical connection of the networks by interlocking some portion of the polymer otherwise disrupting chemical bonds. Without being bound to any theory, the two networks are considered separately "Macromolecules" 1982, 15, 625-631, cannot totally separate the two networks without breaking or extraction, or any other conventional separation processes, such as disclosed in J. M. Widmayer and L. H. Sorkin, "Integrity of one of the networks. Illustratively, high pressure liquid chromatography (HPLC), Sorkin characterized by an inability to totally physically separate one network from the other without breaking the chemical bonds in the presence of a second polymer network. Such polymer network systems may be crosslinked in the immediate presence of one another. Thus, at least one of the polymer networks is formed For the two polymer networks a necessary criterion is that the networks are polymerized and/or accordance with the teachings herein.

45 present. In a preferred mode two networks are present, although three or more can be present in crosslinks. In the present embodiment of the invention it is required that at least two polymer networks are the polymer networks.

The term "network" means a three-dimensional system of polymer chains held together by chemical 40 network composition is capable of being dispersed in an organic solvent and by a method of preparation of that the composition contains at least two polymer networks characterized by the criterion that the polymer of polymerization.

The novel composition of matter differs from the interpenetrating polymer networks of the prior art in 45 interpenetrating mechanisms of polymerization, the mechanisms may have the same or different rates of kinetics polymer networks are formed simultaneously or substantially simultaneously by independently non-polymer networks routes of polymerization as employed in Spelling, P. 423. In the instance when the with non-interpenetrating routes of application, non-interpenetrating mechanisms of polymerization is synonymous employed in the present patent application, non-interpenetrating technology employed herein. As NY, 1989. Therefore, this publication is incorporated by reference for the terminology employed herein. As "Reactions", Edited by G. C. Eastmond, A. Ledwith, S. Russo, and P. Sigwalt, Pergamon Press, Elmsford, forth by L. H. Spelling in pages 423-436 of "Comprehensive Polymer Science", Volume 6, "Polymer to be a new class of an interpenetrating polymer network consistent with the terminology and definitions set The present invention is directed to a novel composition of matter or polymer product which is believed

POLYMER PRODUCT

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DETAILED DESCRIPTION OF THE INVENTION

(ii) the two polymer networks are formed sequentially or substantially simultaneously by independent and non-interpenetrating mechanisms of polymerization.

20 (i) the two polymer networks are formed sequentially wherein the second polymer network is formed in a solvent dispersion of the first formed polymer network, or polymerization in solvent and that one of the following takes place in formation of two polymer networks: (b) are dispersible in a solvent with the proviso that at least one of the polymer networks is formed by (a) are polymerized and/or crosslinked in the immediate presence of one another, and

15 The present invention is directed to a composition of matter comprising at least two polymer networks which

SUMMARY OF THE INVENTION

polymer products, and to improve their end-use performance.

20 convenience polymer binders which have crosslinked or network-like structure for use in coating and produce their utility in photosensitive formulations. There is a need, which is not met by the current technology, to after their formulation they are not soluble or dispersible in photosensitive solvents marketed reduces and semi-interpenetrating polymer networks are desirable in conventional coating solvents that average molecular weight (weight average) of 1,000 to 100,000.

25 a photopolymerizable material suitable for producing printing forms or resist patterns. The polymer binder disclosed consists of a film-forming copolymer that has a two-phase morphology and an average molecular weight (weight average) of more than 10,000. The copolymer is produced using a macromer with an average molecular weight (weight average) of 1,000 to 100,000.

Preferred addition polymerizable monomer precursors include: methyl methacrylate (MMA); ethyl methacrylate (EMA); butyl methacrylate (BMA); 2-ethylhexyl methacrylate; methyl acrylate (MA); ethyl acrylate (EA); butyl acrylate (BA); 2-ethylhexyl acrylate; 2-hydroxyethyl methacrylate (HEMA); ethyl vinyl acetate (S); alpha-methyl styrene; vinyl acetate; vinyl chloride; acrylamide; N-t
maleimide; aminoethyl methacrylate; aminoethyl acrylate; t-butyl aminoethyl methacrylate; acrylamide; N-t
acrylamide; half ester and itaconic imide; maleic acid and maleic anhydride; maleic acid half ester and
acid half ester and itaconic acid; glycidyl acrylate and methacrylic acid; itaconic acid anhydride; itaconic
methacrylic acids; itaconic acid (IA) and itaconic acid anhydride; itaconic
methacrylic group contains from 1 to 18 carbon atoms; nitriles and amides of acrylic and
wherein the alcohol group contains from 1 to 18 carbon atoms; esters of acrylic and methacrylic acids
ethyl acrylate (HEA); methacrylic acid (MAA); acrylic acid (AA); esters of acrylic and methacrylic acids
wherein the alcohol group contains from 1 to 18 carbon atoms; nitriles and amides of acrylic and
methacrylic acids; itaconic acid anhydride; itaconic
methacrylic imide; maleic acid and maleic anhydride; maleic acid half ester and
acid half ester and itaconic imide; glycidyl acrylate and methacrylic acid; itaconic acid anhydride; itaconic
methacrylic acids; itaconic acid (IA) and itaconic acid anhydride; itaconic
methacrylic acids; itaconic acid anhydride; itaconic
acrylamide; vinyl methyl ether; alpha-methyl styrene; vinyl acetate; vinyl chloride;

polymer network and even more preferably between 0.5 and 3 weight %.

example, ethylene glycol dimethacrylate or a triisocyanate or some other multifunctional monomer. Typically the crosslinking precursor comprises less than 10 weight % of the precursors used to form the

(arylene sulfides) and poly(arylene sulfones). The polymer chains can be substantially composed of homopolymer or copolymers, but are crosslinked with conventional crosslinking precursors such as, for

and vinyl alcohols; polyamides; polyimides; polyketones; silicones; polycarbonates; polyesters; polyolefins such as polyethylene and polypropylene; diolefin polymers such as polybutadiene and polylisoprene; and poly-

addition, step-growth or ring-opening polymerization. Illustrative of polymer networks are acrylics; styrenics; phenolics; epoxies; urethane polymers; polyesters; polymers of vinyl halides, vinylidene halides, vinyl esters

range is between 0.5 and 10%. These polymer networks can be any of those prepared in solution by kinetics involved. A preferred range is between about 0.3 and about 1% by weight. A particularly preferred

of crosslinking desired, the nature of the monomeric and crosslinking precursors, and the polymerization mode.

Each constituent polymer network which constitutes the composition of either of the present invention is prepared from two or more soluble monometric precursors, wherein a small percentage of the macromolecules possesses a crosslinking precursor. This small percentage will vary depending on the desired

Each constituent polymer which constitutes the composition of matter of the present invention is not dispersible in conventional solvents or tinsile.

Previous interpenetrating polymer networks is typically continued far beyond the gel point to form a gel that remains in the polymerization process.

Such polymer products may also contain solvent dispersible oligomers, soils, critical gels or combinations thereof, suspending agents, stabilizers, emulsifiers, dispersants, surfactants, and/or crosslinking agents.

is terminated before, subsequently adding polymeric networks, or second polymer networks, in addition to the crosslinked polymer networks.

The composition of this invention, i.e., the polymer product, is dispersible in solvent, and comprises at least two interpenetrating polymer networks, as defined supra, which may include infinite

gel point is called a gel, which is not soluble, even in a good solvent. However, low molecular weight molecules (sol fraction) are still extractable.

The polymer reaches the gel point at a critical extent of the polymerization/crosslinking reaction. The scale. The polymer before the gel point is called a sol because it is soluble in good solvents. The polymer beyond the scale. The polymer reaches the gel point is called a gel because it is insoluble in good solvents. The polymer beyond the gel point is called a crosslinked polymer.

cluster. The molecular motions are correlated over large distances but the critical gel has no intrinsic size distribution is infinitely broad and molecules range from the smallest unreacted oligomer to the infinite cluster.

Second Edition, Wiley & Sons, 1989 (which is incorporated herein by reference) -- a polymer at its gel point, the critical gel, is in a transition state between liquid and solid. Its molecular-weight

Paraphrasing the definition given in pages 343-351, "Encyclopedias of Polymer Science and Engineering" (Supple-

gel point is a well-defined stage in polymerization in which the polymerization transitions suddenly from a viscous liquid to an elastic gel.

Although such networks may be swellable in organic solvent, they remain insoluble and dispersible. The all-polymerized state is well described in which the polymerizable transformations suddenly form a

polymer network which has substantially infinite molecular weight (M_∞) and which is considered to extend throughout the volume of the polymerized material [6]. Approachin the size of the reaction vessel

Conventional interpenetrating polymer networks of the prior art cannot be dissolved or dispersed in such solvents since gel point leads to an interpenetrating network far beyond the gel point.

Examples of aqueous and semiaqueous liquids include water solutions of ammonia, amines, alkanes, alkoxylalkanols, acids, bases and the like.

the networks. While the composition of matter involved typically is formed in an organic solvent, the composition of matter formed may be subsequently dispersed in aqueous or semiaqueous liquids.

An example of a solvent which can conveniently be employed to determine a property of colloids. An example of a solvent for one of the components which serves as a precipitor in the formation of

pointed out that the composition of matter need only be dispersible in one of the solvents to meet this

A solvent is used in its conventional sense with examples of organic solvents including liquid alkanes, A

Although such polymer networks bearing polymer arms are used herein as an intermediate to form the composition of matter of this invention, such unique networks may be used as the sole polymer network or as a simple polymer mixture in a formulated polymer products. Such a polymer network is a composition of matter comprising a polymer network containing at least 0.5% by weight of branch or graft linear polymer segments, wherein the polymer network is dispersible in a solvent and wherein the polymer network is formed by polymerization in a solvent. It is preferred that the branch or graft linear polymer segments are formed by polymerization in a solvent.

members of this committee will be invited to this meeting.

During conventional polymerization of monomer/binder systems, such as in photore sist formulations as described supra, in which the monomer/binder typically plasticizes the polymeric binder, the newly formed polymeric material is believed to separate from the monomer/binder to form distinct microdomains. During the formation of the product of this invention, the tendency to phase separate persists but is significantly retarded due to the interpenetrating network which is hypothesized to interlock at least a portion of one of the constituent networks into a portion of the other network. Thus the product of this invention consists of a single homogeneous domain where no separation occurs, two domains where one network is completely encompassed in a portion of a second network, or multiple domains where each network is encompassed only in a portion of the other. The actual number of domains may be determined, in some instances, by electron microscopy and the mixing of networks from the measured class fraction.

- C =CR₆R₇

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can form a heterocyclic ring);

(where R_2 and R_3 can be hydrogen, alkyl or cycloalkyl of 1-18 carbon atoms, aryl, alkenyl, alkaryl), or together R_2 and R_3 (where R_4 is hydrogen, alkyl or cycloalkyl of 1-18 carbon atoms, aryl, alkenyl, alkaryl, aralkyl) - $\text{CH}_2\text{O}R_4$ (where R_2 and R_3 is hydroxyl or carboxyl group).

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—C-NR₂R₃

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(i) the polymer network and the linear or branched polymer; formation of the polymer network and the linear or branched polymer;

(ii) the polymer network and the linear or branched polymer; subsequent addition wherein, in either order, the polymer network (or the linear or branched polymer) is formed in a solvent solution or dispersion of the first formed polymer (or the polymer network), or

(iii) the polymer network and the linear or branched polymer; formation of the linear or branched polymer and the linear or branched polymer are formed simultaneously or substantially linear or branched polymer formed polymer (or the polymer network), or

An additional embodiment of this invention is a composition of matter comprising at least one polymer network and a linear or branched polymer which are dispersible in a solvent with the proviso that the polymer network is formed by polymerization in a solvent and that one of the following takes place in

between about 0.5 and about 80 weight-% of the precipitates used to prepare the imidized polyimide framework and preferably between about 5 and about 50 weight-%.

to 18 carbon atoms; nitrites and amides of acrylic and methacrylic acids, glycide acrylate and methacrylate esters; itaconic acid anhydride, itaconic acid half ester and itaconic imide; maleic acid and maleic acid anhydride; maleic acid half ester and maleimide; vinyl methyl acrylate; t-butyl aminoethyl methacrylate; acrylamide; N-t-octyl acrylamide; vinyl methyl ether; styrene (S); alpha-

(BMA); 2-ethylhexyl methacrylate; methyl acrylate (MA); ethyl acrylate (EA); butyl acrylate (BA); 2-hydroxyethyl acrylate; 2-hydroxyethyl methacrylate (HEMA); 2-hydroxyethyl acrylate (HEA); methacrylic acid (MAA); acrylic acid (AA); esters of acrylic and methacrylic acids wherein the alcohol group contains from 1 to 6 carbon atoms; and methacrylates and methacrylic acids which contain carboxylic acid groups.

At least one network constituent of the composition of matter of this invention may contain at least one type of polymer arm, but two or more or all polymers may likewise bear polymer arms. The polymer arms attached to the polymer network constituents may likewise bear polymer arms. The type of polymer arm, or the number of arms, or the length of the arms, or the nature of the polymer from which the arms are derived, or the nature of the linkage between the arms and the polymer network constituents, or the nature of the linkage between the arms themselves, or the like, may be selected to provide a polymer having the desired properties.

formed during formation of the polymer network from at least one macromer, linear polymer precursor having a terminal polymethylatable group.

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The composition of matter of the invention may be prepared by polymerizing one set of monomers and/or oligomers (to form polymer network B) into an already formed polymer network A.

Polymer A is first prepared, in an organic liquid which is a solvent for both polymer A chains and suitable initiator and crosslinking agent. Polymerization is continued until the resulting polymer has a weight average molecular weight (M_w) of about 15,000 or more such as 30,000 by gel permeation chromatography (GPC) and is crosslinked with about 0.3 to about 10% by weight of total monomers of a suitable initiator and crosslinking agent. Polymerization is continued until the resulting polymer has a weight average molecular weight (M_w) of about 15,000 or more such as 30,000 by gel permeation chromatography (GPC) and is crosslinked with about 0.3 to about 10% by weight of total monomers of a suitable initiator and crosslinking agent. It is generally preferable that maximum network formation is then added to the liquid containing agent and an initiator or catalyst, Monomer set B, together with about 0.3 to about 10% of a crosslinking agent such as 30,000 as determined by GPC. This second polymerization is carried out so that monomers or oligomers of set B do not form graft copolymers with polymers of the first polymerization.

Times, temperatures, pressures and initiators or catalysts are conventional for the monomers chosen, and polymerizations are carried out so that the resulting dispersion will generally contain less than about 75% solids (total polymers).

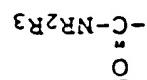
An additional embodiment of this invention is a composition of matter comprising at least three polymer components wherein at least two of the polymer components are polymer networks which are polymerized and/or crosslinked in the immediate presence of one another, and wherein at least two of the polymer networks are dispersible in a solvent with the proviso that at least one of the solvent dispersible polymer networks is formed by polymerization in a solvent and that one of the solvent dispersible polymer networks is formed by polymerization of the remaining polymer component(s) in a solvent subsequent to the formation of the two solvent dispersible polymer networks. The remaining polymer component(s) may be a linear or branched polymer, wherein the remaining polymer component(s) is formed subsequent to the formation of the two solvent dispersible polymer networks. The remaining polymer component(s) is formed by independent solvent dispersing mechanisms of polymerization; and

(i) the two polymer networks are formed sequentially wherein the second polymer network is formed in the two solvent dispersion of the first formed polymer network, or

(ii) the two polymer networks are formed simultaneously or substantially simultaneously by independent solvent dispersing mechanism of polymerization;

wherein the two non-interacting polymer component(s) is formed simultaneously by independent solvent dispersing mechanism of polymerization.

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(where R_5 , R_6 and R_7 can be hydrogen, alkyl or cycloalkyl of 1-18 carbon atoms, aryl, alkaryl, aralkyl).

specroscopy, with the results analyzed by customary statistical methods. The analysis is performed at 55 samples withdrawn from any point in the dispersion. Statistical homogeneity is determined from 55 chains, when concentrated or diluted to 55% solids, and when held over a period of seven days at 25°C. To keep the statistical homogeneity of the composition of its dispersed phase, within ±10%, as determined by conventional analytical techniques such as Fourier Transform infrared Spectroscopy or NMR analysis by conventional analytical techniques such as Fourier Transform infrared Spectroscopy or NMR.

"Stabilized" is the property shown by a dispersion, in a good solvent for all the constituent polymer polymers to remain in intimate contact on a microscopic scale.

"Compatibility" is used herein in the conventional sense of meaning the property of two or more bonds need exist between the atoms of one network and those of another.

"Catenated", as it is used herein, means the connection of the networks by the interlocking of some portion of those networks so that physical separation, as determined by high pressure liquid chromatography (HPLC), is not possible without breaking or otherwise disrupting the networks. No actual chemical crosslinks.

By "network" is meant a three-dimensional system of polymer chains held together by chemical crosslinks, and whose dispersions are stabilized by the networks being catenated.

A dispersion of the invention is composed of at least two incompatible polymer networks which are connected in turn, is composed of a dispersed phase in an organic liquid. This dispersed phase, in turn, is composed of the dispersed phase superior to those of the prior art.

This stability is due to the presence of the dispersed phases of catenated networks of the constituent polymers. The catenation not only stabilizes the dispersions but in many cases also gives, in products derived from these dispersions, properties superior to those of the prior art.

These dispersions do not separate on standing, but also in the sense that these phases keep their homogeneity over long periods. All this is accomplished without the use of extrinsic stabilizers.

The dispersions of the present invention, in contrast, are stable not only in the sense that their dispersions do not separate on standing, but also in the sense that they separate into two layers or phases on standing unless they have been stabilized by a sufficient quantity of a block copolymer or graft polymer produced in (a).

In the past, attempts to prepare blends of two or more incompatible polymers in a compatible organic liquid have given dispersions which are unstable in the sense that they separate into two layers or phases on standing unless they have been stabilized by a sufficient quantity of a block copolymer or graft polymer produced in (a).

The organic liquid being a common solvent for the polymer chains produced in (a) and (b), and the polymerization conditions in (b) being such that the monomers do not form graft copolymers with the

of (a) and polymerizing these monomers into the network produced in (a); to the product (b) adding one or more sets of monomers, together with a suitable crosslinking agent(s), to the product

(a) preparing a polymer network in an organic liquid by polymerizing a set of monomers in contact with a suitable crosslinking agent; and then

The present invention further provides a process for the preparation of the above dispersions comprising:

above.

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above.

POLYMER DISPERSIONS

solder mask formulation, and exposing it to actinic radiation.

product of this invention into a photopolymerizable system containing crosslinking monomers, such as a

multiple interpenetrating polymer networks is by incorporating a soluble dispersible two-polymer network

As will be described in detail subsequently, a preferred process for forming this unique class of triple or

polymer component is a polymer network, a triple or multiple interpenetrating polymer network is formed.

forming the polymer networks at least two normally incompatible polymer networks which are

matter of this invention is formed. Specifically, the instant invention provides a dispersion, in an organic

in yet an additional embodiment of this invention a stable solvent dispersion of the composition of

multiple components for forming linear, branched or network polymers as well as the process of

including conventional processes for forming linear, branched or network polymers as well as the process of

multiple components for forming linear, branched or network polymers as well as the process of

multiple components for forming linear, branched or network polymers as well as the process of

multiple components for forming linear, branched or network polymers as well as the process of

multiple components for forming linear, branched or network polymers as well as the process of

25	The dispersions of the invention are obtained by evaporating the dispersion to dryness.	The dispersions of the invention are obtained by a sample obtained from organic liquids. Any organic liquid can be used which is compatible with the system, i.e., one which does not adversely affect the physical or chemical characteristics of the constituent polymer chains or their networks to any significant degree. In the preparation of the dispersions, a liquid should be selected which is a good solvent for all the constituent polymer chains. For diluting the dispersions after they have been prepared, it is necessary that the liquid be a solvent for at least one of the polymer chains.
30	25. C and is performed on a sample obtained by N,N-dimethylacetamide and dimethylsulfoxide. Mixtures can also be used.	25. C illustrates the use of organic liquids which can be used are aromatic and aliphatic hydrocarbons, ketones, alcohols, ethers, alcohol ethers, esters, chlorinated hydrocarbons and aromatic solvents such as N-methylpyrrolidone, N,N-dimethylacetamide and dimethylsulfoxide. Mixtures can also be used.
35	1. The polyacrylic acid ester, polyesters, polyamides; polymers of vinyl halides; vinylidene methacrylate or ring-opening polymerization. Illustrative are acrylics such as acrylate or methacrylate polymers; polyesters and vinyl alcohols; polyesters; polyamides; silicones polymers; vinylidene halides; vinyl esters and vinyl ethers; epoxides; urethane polymers; polymers of vinyl halides; vinylidene halides, step-growth or ring-opening polymerization. Illustrative the catenated systems can be any of those prepared by addition, provided that the following conditions are met:	1. The respecitive preparrative polymerizations must be capable of occurring sequentially or concurrently without interfering with each other.
40	2. The respecitive preparrative polymerizations must be capable of occurring sequentially or concurrently without interfering with each other.	2. The respecitive preparrative polymerizations must be capable of occurring sequentially or concurrently without interfering with each other.
45	3. Solutions of monomers and oligomers of the catenated systems must be incompatible with one another in the absence of the other.	3. Solutions of monomers and oligomers of the catenated systems must be incompatible with one another; or monomers used to make one polymer network must be able to swell the polymer network of the other.
50	4. S/EA/EGDMA-MAA-HEMA/EGDMA/MAA	4. S/EA/EGDMA-MAA-HEMA/EGDMA/MAA
55	5. S/B/A/EGDMA-MAA-DEADM-VP/HEMA/EGDMA	5. S/B/A/HEMA-MAA-DEADM-VP/HEMA/EGDMA
60	6. PEU network-Acrylic network	6. PEU network-Acrylic network
65	7. PEU network-PEU-PVAc network	7. PEU network-PEU-Acrylic network
70	8. PEU network-PEU-PVAc network	8. PEU network-PEU-Acrylic network
75	9. PEU network-VP-PV network	9. PEU network-VP-PV network
80	10. Epon/S/EMA-MAA/Uunsaturated PE	10. Epon/S/EMA-MAA/Uunsaturated PE
85	In the foregoing, the symbols have the following meanings:	In the foregoing, the symbols have the following meanings:
90	EGDMA = ethylene glycol dimethacrylate	EGDMA = ethylene glycol dimethacrylate
95	MMA = methyl methacrylate	MMA = methyl methacrylate
100	AA = acrylic acid	AA = acrylic acid
105	BA = butyl acrylate	BA = butyl acrylate
110	S = styrene	S = styrene
115	HEMA = hydroxymethyl methacrylate	HEMA = hydroxymethyl methacrylate
120	DEAM = diethylaminoethyl methacrylate	DEAM = diethylaminoethyl methacrylate
125	PE = polyester	PE = polyester
130	PEU = polyurethane polymer	PEU = polyurethane polymer
135	MAA = methacrylic acid	MAA = methacrylic acid
140	PVAc = poly(vinyl acetate)	PVAc = poly(vinyl acetate)
145	Acrylic = polymer or copolymer of an acid, amide, ester or nitrile of acrylic or methacrylic acid	Acrylic = polymer or copolymer of an acid, amide, ester or nitrile of acrylic or methacrylic acid
150	V-P-vinyl pyridine	V-P-vinyl pyridine

(a) a composition of matter of this invention, and
A sensitive composition of this invention comprises:
soldier masks, and the like, which will be further described to illustrate this invention.
useful in sensitive compositions and in particular in photoresistive compositions such as photoreists,
The polymer products, i.e., compositions of matter and dispersions, of this invention are particularly
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SENSITIVE COMPOSITIONS

epoxies, isocyanates and amineplast resins.
crosslinking one or more of the constituent polymer networks with such external crosslinking agents as
superior toughness flexibility balance and solvent resistance can be built into the residues by further
can be used as elastomers, can be used in the fabrication of gaskets, hoses, belts and bushings, and as
aircraft and automobile products. The residues can also be extruded or molded into various useful shapes,
photoreists and as soldier masks and for the formation of curved panels of various plastic materials in
panels, as mold release films, as adhesive films, e.g., for the manufacture of multilayer printed circuits, as
and for use in electrolytic cells, as mar-resistant tough films for structural automobile parts and building
this invention, can be used to make films useful as semi-permeable membranes for the purification of water
40 The residues from removal of the organic liquids from the dispersions, i.e., the composition of matter of
with conventional solvents to allow for ease of replacement or repair.

45 The residues are especially useful for applying mar-resistant finishes to make coatings for industrial
cosmetic and automotive purposes. They are especially useful for applying mar-resistant finishes to
automobile and truck parts, for coating plastic automobile parts and as pigments dispersants. The dispers-
ions are also useful as nail coatings having keratin as the primary proteinaceous constituent. The nail coating
composition therefore, having dispersed or dissolved therein a polymer product of this invention. The nail coating
comprises an organic solvent, e.g., toluene, ethanol, ethyl acetate, butyl acetate, and combinations
of cellulose substrates having keratin as the primary proteinaceous constituent. The nail coating
other such compositions are also useful as nail coatings such as polish or enamel for fingernails or toenails or
automobile and truck parts, for coating plastic automobile parts and as pigments dispersants. The dispers-
ions are also useful as nail coatings having keratin as the primary proteinaceous constituent. The nail coating
50 The residues of about 40-60% (total catalyst polymer system).
contents of about 40-60% (total catalyst polymer system).

55 The residues are especially useful for graft copolymer agent. The resulting dispersions have solids
weight of total monomers of a polyfunctional crosslinking agent. The resulting dispersions have solids
as a molecular weight M_w of about 30,000 or more by GPC and is crosslinked with about 0.5-10% by
instances different. As in the sequential method, polymerizations are continued until each polymer network
must be selected so that the respective rates of polymerization are approximately the same and in some
polymerization. The polymerizations are conducted conventionally, but conditions and initiators or catalysts
non-interfering. For example, one could be a free-radical polymerization and the other, a condensation
liquid. The sets are then polymerized simultaneously, but the types of polymerization must be diverse and
polymers of Set B and appropriate crosslinking agents for each set are dissolved in a common organic
in the concurrent method, the monomers and/or oligomers of Set A and the monomers, oligomers and
are carried out so that the resulting dispersion will contain about 40-60% solids (total polymers).

60 Times, temperatures and pressures are conventional for the monomers chosen, and the polymerizations
that monomers or oligomers of set A do not form graft copolymers with polymer network B.
Monomer set A, together with about 0.5-10% of a crosslinking agent and an initiator or catalyst, is
then added to the liquid and polymerized until the molecular weight M_w of polymer network A is about
that maximum network formation shot of macrogelation be obtained during this stage.

65 the resulting polymer has a molecular weight M_w of about 30,000 or more by GPC and is
monomers and/or oligomers in contact with a suitable crosslinking agent. Polymerization is continued until
solvent for both polymer A chains and polymer B chains, by conventionally polymerizing the desired
in the sequential method, a network of polymer B is first prepared, in an organic liquid which is a good
solution. The sequential method is preferred.

70 They may also be formed by concurrent polymerizing sets of monomers (one set to form polymer
oligomers (to form polymer network A) into an already formed polymer network B), a sequential operation.
The dispersions of the invention can be prepared by polymerizing one set of monomers and/or
The systems preferred for use in the dispersions are numbered 1-7 in the foregoing list.

In those instances when a latent image is formed, the exposed or unexposed areas of the layer containing the latent image may be then modified by removing exposed or unexposed areas, depositing a material on or in the exposed or unexposed areas or further treating the layer; so developing a material or in the exposed or unexposed areas of the layer to form a deep relief image which the exposed or unexposed areas adhered to the substrate. A deep relief image in compilatory unexposed or aqueous alkaline developers either a deep relief from the stencil image with solvent or aqueous alkaline developers they may be peeled from the stencil image.

Applications requiring no additional processing steps after exposure to actinic radiation, include, those where an image is formed directly, e.g., photopolymer holograms as disclosed in Haug U.S. Patent 3,658,526 wherein the refractive index changes upon exposure to actinic radiation, diffusion resists as in Gervey and Walker U.S. Patent 3,718,473, color forming systems as in Cescoson and Dessauer U.S. Patent 3,445,234 or other photochromic systems. Color forming systems based on photooxidizable or photoreduced, e.g., a photoresist screen printing ink as in Lipszon et al. U.S. Patent 4,003,877.

Typically the photosensitive compositions of this invention are used in the form of a supported film or layer although unsupported solid objects may also be prepared. The photosensitive composition is applied to a suitable substrate to form a continuous film or layer thereon which is imagewise exposed to actinic radiation to form an image directly or latent image. Alternatively, the layer may be uniformly exposed to actinic radiation to cure or harden the layer when the photosensitive composition is applied in form of a continuous or patterned layer such as a protective finish, a paint or ink. Any conventional source of actinic radiation may be used including arc, discharge, and incandescent lamps as well as lasers, X-ray and electron beam units. The layer may be applied as a neat, solvent-free, photosensitive liquid or as a dispersion or solution and dried to a solid layer wherein any conventional coating or printing process may be used. Alternatively, the layer or film may be applied by laminating a supporting or unsupported solid dispersion or solution or solid to the substrate and then optionally removing the support.

Although the polymer product itself may be photoactive, generally a photoresistive composition contains one or more photoactive components in addition to the polymer product. Upon exposure to actinic radiation, the photoactive component acts to change the rheological state. The surface characteristics, refractive index, the color, the electromagnetic characteristics, or other physical or chemical characteristics of the photoresistive composition, such as described in the Netherette's publication above

The polymer products of this invention are useful as components of photosenstive systems and particularly in photomasking systems such as those described in "Light-Sensitive Systems: Chemistry and Application of Nonsilver Halide Photographic Processes" by J. Kosar, John Wiley & Sons, Inc., 1965 and more recently in "Imaging Photographic Processes" by J. Kosar, John Wiley & Sons, Inc., 1965 and Walworth and A. Shepp, Van Nostrand Reinhold, 1969. In such systems, actinic radiation impinges on a material containing a photoactive component to induce a physical or chemical change in that material. A useful image or latent image which can be processed into a useful image thereby produced. Typically actinic radiation useful for imaging is light ranging from the near ultraviolet through the visible spectrum, but in some instances may also include infrared, deep-ultraviolet, X-ray and electron beam radiation.

EP 0 501 433 A1

The polymer products of this invention are particularly useful in photopolymerizable compositions which contains a monomeric material and a photoinitiator system. In such systems the polymer product functions as a dispersible polymeric binder component to impart desired physical and chemical characteristics to the exposed and unexposed photopolymerizable composition. Upon exposure to actinic radiation, the photoinitiator system induces chain propagation polymerization of the monomeric material by either a condensation mechanism or by free radical addition polymerization. While all photopolymerizable mechanisms are contemplated, the compositions and processes of this invention will be described in the context of free radical initiation polymerization of monomers having one or more terminal ethylenically unsaturated groups. In this context, the photoinitiator system when exposed to actinic radiation acts as a source of free radicals needed to initiate polymerization of the monomer. The photoinitiator of the system may be activated by a photosensitizer which absorbs actinic radiation which may be outside the absorption spectrum of the initiator itself, to sensitize the addition polymerization in more practical radiation spectral regions such as near ultraviolet, visible light and near infrared. In the narrow sense, the term photoinitiative composition of this invention refers to the material which absorbs the actinic radiation, e.g., the photoinitiator or the photosensitizer, but in the broader sense the term photoinitiative composition refers to any or all the essential materials needed for photopolymerization, i.e., the photoinitiating system

PHOTOPOLYMERIZABLE COMPOSITIONS

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areas is developed into an image of latent image by spectrogram readout and a grayscale image by A. illustrative of such photosensitive systems are those described in Chapter 7, "Polymer Imaging" by B. Cohen and P. Walker in Nebelte's *Supra*, pages 226-262, in which photocrosslinking, photodimerization, photocyclization, photosolubilization, and both ionic and free radical photopolymerization, as well as electron-stabilized photopolymer imaging are discussed. In Chapter 8, "Low Amplification Imaging Systems" by R. Desseuder and C. E. Looney, pages 263-278, imaging systems discussed include color forming free radical, diazo, and vesicular systems, photochromism, phototackification and photodetackification as well as thermal and photothermal systems.

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sides of the relief are tapered and do not extend to the substrate, typically is used as a letterpress or flexographic printing plate, e.g., as disclosed in U.S. Patent 2,760,863 and Brennen and Chen subsurface thereby forming complimentary uncoupled substrate surface areas. A stencil image has numerous applications, e.g., as a resist as disclosed in Gelelite U.S. Patent 3,498,982, as a lithographic printing plate and U.S. Patent 4,247,619. When a stencil image is formed and is used as a resist, unprotected substrate areas are formed which may be further modified by etching the unprotected surface areas or deposited by material thereon. The exposed or unexposed areas of the layer containing the latent image may be modified by depositing a material such as a phototackification process wherein powdered Gross U.S. Patent 4,604,340. Liquid toners are also used in electrostatic systems to develop latent images in a photoconductive corona photoinensitive process such as disclosed in Riesenfeld et al. U.S. Patent 4,732,831. Photomagnetic and photodemagnetic systems are used to apply dye to fabrics and resists to circuit boards as disclosed in Gorondy U.S. Patent 4,105,572, Nacci U.S. Patent 4,292,120 and Nacci et al. U.S. Patents 4,338,391 and 4,359,516. Photosensitive compositions containing a latent image may also be developed into an image by treatment with a developer reagent. In some silver halide direct-writing systems, a visible image upon treatment with a diazotype developer forms a latent image upon exposure which is developed into a visible image by further treatment with a developer reagent. In some silver halide direct-writing systems, a visible image upon treatment with a diazotype developer forms a latent image upon exposure which is developed into a visible image by further treatment with a developer reagent. Such reversal systems also include photodesensitized areas, e.g., as disclosed in U.S. Patent 3,778,270. Such reversal systems also include photodesensitized areas, e.g., as disclosed in U.S. Patent 4,477,556, containing a photoinhibitor wherein imaging exposure to actinic radiation generates inhibitory in the exposed areas of the layer and a subsequent uniform heat, or in some instances uniformly heated, generates a latent image in the complementary areas free of photogenenerated inhibitor. Such reversal systems also include photopolymer systems, e.g., as disclosed in U.S. Patent 4,198,242 or Duerber et al. U.S. Patent 4,477,556, containing a photoinhibitor wherein imaging exposure to actinic radiation generates inhibitory in the exposed areas of the layer and a subsequent uniform heat, or in some instances uniformly heated, generates a latent image in the complementary areas free of photogenenerated inhibitor in the layer and a subsequent uniform heat.

4,772,534 and 4,774,163. A useful discussion of dye sensitized photopolymerization can be found in "Dye complexes disclosed in U.S. Patent 4,772,541; and trichloromethyl triazinones disclosed in U.S. Patents 3,549,367; 4,311,783; 4,622,286; and 3,784,557 can be used as initiators. Other initiators are dye-borate dimers with hydrogen donors, and mixtures thereof as described in U.S. Patents; 3,427,161; 3,479,185; as well as dyes of the phenazine, oxazine, and quinone classes; ketones, quinones; 2,4,5-triphenoxyimidazole disclosed in U.S. Patents; 2,850,445; 2,875,047; 3,097,096; 3,074,974; 3,097,097; 3,145,104; and 3,579,339. A large number of free-radical generating compounds, including redox systems such as Rose Bengal/2-dibutylaminethanol, may be selected to advantage. Photoreducible dyes and reducing agents such as those disclosed in U.S. Patents; 2,850,445; 2,875,047; 3,097,096; 3,074,974; 3,097,097; 3,145,104; and 3,579,339, sensitizer that extends spectrally into the near ultraviolet, visible, and near infrared regions.

50 Curing the compound to furnish the free-radicals. Useful photoinitiator that is activated by the actinic radiation, by actinic radiation. The system also contains a sensitizer that is activated by the actinic radiation, causing the compounds to furnish free-radicals. Useful photoinitiator systems typically will contain a sensitizer that extends spectrally into the near ultraviolet, visible, and near infrared regions.

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PHOTONITIATOR SYSTEMS

A particularly preferred class of monomers are t-butyl acrylate, cyclohexyl acrylate, hydroxy C₁-C₁₀-alkyl acrylate, butanediol diacrylate, hexamethylene diacrylate, trimethylene glycol diacrylate, tripropylene glycol diacrylate, pentaacryl triacrylate, hexamethyleneglycol diacrylate, trimethylolpropane triacrylate, pentaacryl triacrylate, dihydroxy-2-hydroxypropyl ether of tetraacryloyl bisphenol-A, or methacrylate analogues thereof.

40 A particularly preferred group, especially the vinylidene groups, are conjugated with ester or amide structures. Unsatuated groups, especially the vinylidene groups, are conjugated with ethylenic linkages. Preferred are such materials wherein the ethylenic linkages are conjugated with a double bonded carbon, including carbon double bonded to carbon and to such heteroatoms as nitrogen, oxygen, and sulfur. Also preferred are such materials wherein most of such linkages are terminal linkages. Preferred are those wherein at least one and preferably most of such when present as terminal linkages. Preferred are addition polymerizable ethylenic linkages particularly U.S. Patent 2,927,222, e.g., those having a plurality of addition polymerizable alkylene linkages particularly glycol of 2 to 15 carbons or a polyalkylene ether glycol of 1 to 10 ether linkages, and those disclosed in styrene, 1,4-benzenediol dimethacrylate, 1,4-diisopropenyl benzene, and 1,3,5-trisopropenyl benzene.

45 A class of monomers are an alkylene or a polyalkylene ether glycol diacrylate prepared from an alkylene methacrylate, trimethylol propane trimethacrylate, 1,5-pentanediol dimethacrylate, diallyl fumarate, tetramethacrylate, pentaacryl triacrylate, 1-phenoxy-1,2-dimethacrylate, penterythritol dimethacrylate, 1,3-propanediol dimethacrylate, 1,2,4-butanetriol trimethacrylate, 2,2,4-trimethyl-1,3-pentanediol trimethylol propane triacrylate (462), ethylene glycol dimethacrylate, butylene glycol dimethacrylate, one trimethylol propylene glycol dimethacrylate, trimethylol propylene glycol dimethacrylate, polyoxypropyl methacryloyx-2-hydroxypropyl ether of diphenolic acid, ether of 1,4-butanediol, di-(3-

50 bisphenol-A, di-(3-methacryloyx-2-hydroxypropyl) ether of tetraacryloyl bisphenol-A, di-(2-methacryloyoxyethyl) bisphenol-A, di-(3-methacryloyx-2-hydroxypropyl) ether of bisphenol-A, di-(3-acryloyx-2-hydroxypropyl) ether of bisphenol-A, di-(2-acryloyoxyethyl) ether of bisphenol-A, di-(3-acryloyx-2-hydroxypropyl) ether of bisphenol-A, di-(2-methacryloyoxyethyl) ether of bisphenol-A, di-(3-methacryloyx-2-hydroxypropyl) ether of bisphenol-1,2-di-(p-hydroxyphenyl)-propane dimethacrylate, trimethylene diacrylate, pentaacryl triacrylate, 2,2-di-(p-hydroxyphenyl)-propane (p-hydroxyphenyl)-propane triacrylate and similar compounds as disclosed in U.S. Patent 3,380,331, 2,2-di-

55 propane triacrylate and trimethacrylate trimethylolpropane triacrylate, pentaacryl triacrylate, trimethylol-glycidol diacrylate, 2,2-dimethylolethane diacrylate, glycidol dimethacrylate, 1,4-cyclohex-panediol diacrylate, decamethylene glycol diacrylate, hexamethylene glycol diacrylate, 1,3-pro-

60 crylate, 1,4-butanediol diacrylate, diethylamine-N,N-diethylaminoethyl-acrylate, ethylene glycol diacrylate, following: t-butyl acrylate, 1,5-pentanediol diacrylate, diethylamine-N,N-diethylaminoethyl-acrylate, and the monomer.

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ADDITION POLYMERIZABLE MONOMERS

Suitable monomers which can be used as the sole monomer or in combination with others include the following point above 100° C at normal atmospheric pressure ethylenically unsaturated compound having a boiling point above 100° C at least one monosubstituted triacylate, glycidol diacrylate, and the monomer.

5 Photopolymerizable compositions contain the polymer products of this invention, an initiating system activated by actinic radiation, and at least one monosubstituted triacylate, glycidol diacrylate, and the monomer.

Cationic photopolymerization is a process to allow concurrent crosslinking during the photopolymerization process.

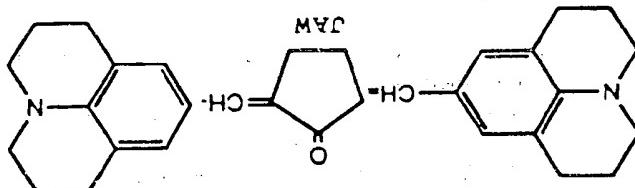
With two, three or more acrylate or methacrylate groups to allow concurrent crosslinking the cationic acrylates or methacrylates and particularly preferred are such compositions containing monomers photoinitiated addition polymerization. Preferred photopolymerizable compositions contain mono or polyfunctional acrylates or methacrylates and being capable of forming a high polymer by polymerization.

Hydrogen donor compounds that function as chain transfer agents in the photopolymer compositions include: 2-mercaptopbenzoxazole, 2-mercaptopbenzothiazole, 4-methyl-4H-1,2,4-triazole-3-thiol, etc.; as well as various types of compounds, e.g., (a) ethers, (b) esters, (c) alcohols, (d) compounds containing allylic or benzylidene groups, (e) acetals, (f) aldehydes, and (g) amides disclosed in column 12, lines 18 to 58 of 55

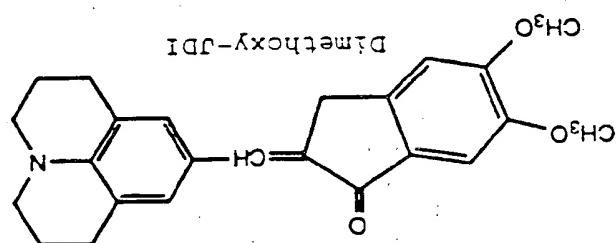
Hydrogen donor compounds in the photopolymer compositions that function as chain transfer agents in the photopolymer compositions include: 2-mercaptopbenzoxazole, 2-mercaptopbenzothiazole, 4-methyl-4H-1,2,4-triazole-3-thiol, etc.; as well as vinylidene(ethylene), CAS 27714-25-6.

Other particularly useful sensitizers are cyclopentanone, 2,5-bis[2-(1,3-dihydro-1,3,3-trimethyl-2H-indol-2-

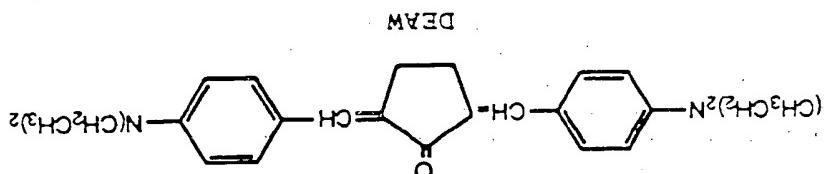
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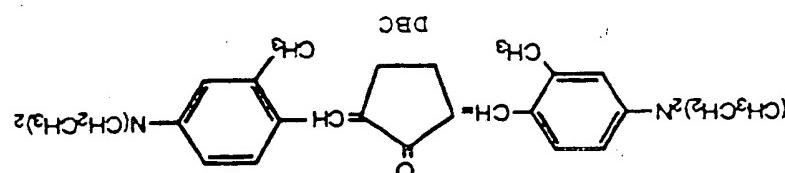
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Sensitizers useful with photoinitiators include methylene blue and those disclosed in U.S. Patents 4,535,052; and 4,565,769. A preferred group of sensitizers include the bis(p-diakylaminobenzylidene) 10 ketones disclosed in Baum et al. U.S. Patent 3,652,275, and the arylidene aryl ketones disclosed in Dubeer U.S. Patent 4,162,162. Preferred sensitizers include the following: DBC, i.e., cyclopentanone; 2,5-bis-[4-methyleno)-2-methylphenyl]-methylene]; DEAW, i.e., cyclopentanone; 2,5-bis[4-(diethylamino)-phenyl]-methylene]; dimethoxy-JDI, i.e., 1H-Inden-1-one; 2,3-dihydro-5,6-dimethoxy-2-(2,3,6,7-tetrahydro-1H,5H-methylenes); benzo([j]-quinolin-9-yl)methylene]; and JAW, i.e., cyclopentanone, 2,5-bis[(2,3,6,7-tetrahydro-1H,5H-

benzo([j]-quinolin-9-yl)methylene], which have the following structures respectively:

Preferred photoinitiators include CD-M-HABI, i.e., 2-(o-chlorophenyl)-4,5,5-tetraphenyl-, dimer, each of which is typically used with 5 dimer; o-Cl-HABI, i.e., 1,1'-biphenyl-4,4'-dimethoxyphenyl-, dimer, each of which is typically used with 1H-imidazole, 2,5-bis(o-chlorophenyl)-4-[3,4-dimethoxyphenyl]-, dimer, each of which is typically used with 10 1H-imidazole, 2,5-bis(o-chlorophenyl)-4,4',5,5'-tetraphenyl-, and TCTM-HABI, i.e., 2-(o-chlorophenyl)-4,5-bis(methoxyphenyl)-imidazole.

Adiencone compounds of U.S. Patent No. 4,341,860 are useful as initiators.

Sensitized Photopolymerization" by D. F. Eaton in Adv. in Photochemistry, Vol. 13, D. H. Voldman, G. S. Hammond, and K. Goilnick, eds., Wiley-Interscience, New York, 1986, pp. 427-487. Similarly, the cyclohex-

POLYMERIC MODIFIERS

CROSSLINKING AGENTS

MacLachlan U.S. Patent 3,901,996. Suitable donor compounds for use in systems containing both bimicazole type initiator and N-vinyl carbazole are 5-chloro-2-mercaptobenzotiazole; 2-mercaptobenzotiazole; 1H-1,2,4-triazole-3-thiol; 6-ethoxy-2-mercaptobenzotiazole; 4-methyl-4H-1,2,4-triazole-3-thiol; 1-dodecanethiol; and mixtures thereof. A particularly preferred class of photoinitiators and photosensitizers are benzophenone, Michler's ketone, ethyl Michler's ketone, p-diakylaminoazobdehydes, p-diakylaminobenzotiazole alkyl esters, polymeric quinones, thioxanthones, hexaarylylimidazoles, cyclohexadienes, benzoin, benzoin dialkyl ethers, or combinations thereof where alkyl contains 1 to 4 carbon atoms.

OPTIONAL COMPONENTS

The photopolymerizable compositions may also contain particulates such as organic or inorganic filters to modify the mechanical properties required during its processing or end use. Suitable filters to include organic reinforcing agents which are essentially transparent as disclosed in U.S. Patent 2,760,863, e.g., organophilic silica dentonite, silica, and powdered glass having a particle size less than 0.4 mil; inorganic thixotropic materials as disclosed in U.S. Patent 3,525,615 such as Boehmite alumina, clay mixtures of highly thixotropic silicate oxide such as bentonite and finely divided thixotropic gel containing 55 3,754,920 such as microcrystalline cellulose and microcrystalline silicas, clays, alumina, bentonite, kaolinites, 99.5% silica with 0.5% mixed metallic oxide; microcrystalline thickeners, as disclosed in U.S. Patent 3,754,920 such as microcrystalline cellulose and microcrystalline silicas, clays, alumina, bentonite, kaolinites,

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FILERS

hexyl) phosphatate, Brige 30 [$\text{C}_{12}\text{H}_{25}(\text{OCH}_2\text{CH}_2)_4\text{OH}$], and Brige 35 [$\text{C}_{12}\text{H}_{25}(\text{OCH}_2\text{CH}_2)_2\text{OH}$]. Isopropyl sebacate, dibutyl sebacate, diocetyl phthalate, tributyl phosphate, tricresyl phosphate, triis(2-ethyl-hexyl) sebacate, dibutyl sebacate, diisopropyl laophthalene, poly(propylene glycol), glyceryl tributylrate, diethyl adipate, ethylhexanoate, tetraethylene glycol dihexanoate, poly(ethylene glycol), poly(ethylene glycol) methyl ether, dipropionate, triethylene glycol dicaprylate, triethylene glycol dimethyl ether, triethylene glycol bis(2-40 40

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Suitable plasticizers include glycol diacetate, triethylene glycol diacetate, triethylene glycol diethyl ether, hardness, solubility, and other mechanical properties required during its processing or end use.

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The photopolymerizable compositions may also contain a plasticizer to modify adhesion, flexibility,

PLASTICIZERS

copolymers, and amphoteric polymers and copolymers. A particularly preferred class of polymers are polystyrene polymers and not exposed to radiation without substantially adversely affecting the integrity of the exposed areas. Patent 4,273,857. Useful amphoteric binders include vinyl pyrrolidone polymers and aqueous solutions containing 1% sodium carbonate by weight, the photosensitive layer will be removed in portions which are disclosed in U.S. Patent 4,293,635. For development in an aqueous liquid, such as wholly aqueous solutions methacrylamides, acidic film-forming comonomer and an alkyl or hydroxalkyl acrylate such as those aqueous-processable polymer additives disclosed in U.S. Patent 3,458,311 and in U.S. sufficient acidic or other groups to render the photosensitive processable in aqueous developer. Useful product of this invention and other polymeric materials in the photosensitive composition should contain in the case where aqueous development of the photosensitive composition is desirable, the polymer acetate, e.g., polyvinyl butyral, polyvinyl formal, polyformaldehydes.

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Cellulose ethers, e.g., methyl cellulose, ethyl cellulose and benzyl cellulose; polyvinyl cellulose; cellulose esters, e.g., cellulose acetate, cellulose acetate succinate and cellulose acetate butyrate; C₁₆-C₁₈ unsaturated fatty acids; vinyls or polyamides, e.g., N-methoxy methyl polyhexamethylenediamide; and alkyl dicarboxylic acid such as succinic, adipic, azelic, sebacic, and dodecanoic acids, and dimers of hexahydroterephthalic, hexahydrosophthalic, hexahydrosoothphthalic, terephthalic, isophthalic, orthophthalic, trimethylol propane, pentamethylol ethane, and trimethylol ethane, together with one or more of the following acids: and trimethyl hexamethylene glycol isomers, and/or polyols with functionality greater than two, such as to 10 inclusive, and/or substituted or branched glycols, such as neopenetyl glycol, 2-methyl-1,3-propanediol, the reaction of at least one poly(methylene glycol) of the formula $\text{HO}(\text{CH}_2)_n\text{OH}$, where n is a whole number 2 average molecular weight from 500 to 1,000,000; epoxides, copolyesters, e.g., those prepared from styrene/butadiene/styrene, styrene/isoprene block copolymers; polyalkylether glycols having methacrylate/acrylonitrile/butadiene/styrene copolymers, 2-chlorobutadiene-1,3 polymers, chlorinated rubber, polyurethanes; synthetic rubbers, e.g., butadiene/acrylonitrile, acrylonitrile/butadiene/styrene, polyvinyl pyrrolidone and copolymers, e.g., poly(vinyl chloride/vinyl acetate); saturated and unsaturated chloride/vinyl acetate copolymers; polyvinyl chloride and copolymers, e.g., poly(vinyl chloride/vinyl acetate); copolymers, e.g., vinylidene chloride/acrylonitrile; vinylidene chloride/methacrylate polymers and copolymers, e.g., with maleic anhydride and esters; vinylidene chloride/vinyl acetate copolymers; polyisobutylene and copolymers, e.g., poly(vinyl acetate) and copolymers, e.g., poly(vinyl chloride/vinyl acetate); polyacrylate and hydrolyzed polyvinyl acetate; polyvinyl acetate/acrylate; polyvinyl methacrylate and acetate/methacrylate and hydrolyzed polyvinyl acetate, polyvinyl acetate/acrylate, polyvinyl with the polymer product of this invention include:

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The photopolymerizable composition may contain other polymeric binders to modify adhesion, flexibility, hardness, oxygen permeability, moisture sensitivity and other mechanical properties required during its processing or end use. Suitable polymeric binders which can be used in combination

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The photopolymerizable compositions of this invention are particularly useful as photoresists for preparing printed circuit boards. In general the use of resists to prepare printed circuits for "Printed Circuits Handbook", Second Edition, edited by C. F. Coombs, Jr., published by McGraw-Hill, Inc. in 1979 which includes both screen printed resists as well as photoresists. The use of conventional photoresists for preparing photoresist circuits is described in "Photoresists-Materials And Processes", published by McGraw-Hill, Inc. in 1975 which includes negative working photopolymerizable photoresists for preparing photoresist circuits as described in "Photoresists-Processes", by W. S. DeForest, published by McGraw-Hill, Inc. in 1975 which includes positive working photopolymerizable photoresists for dimerizable systems as well as possible working photopolymerizable systems. Photoresists may be used in temporary coatings in a primary imaging process to make the printed circuit or they may be used in a secondary imaging process to make permanent coatings, e.g., a solder mask, to protect the circuit during subsequent processing or from environmental effects during use. Permanent coatings also are used as intermediate insulative layers in the manufacture of multilayer printed circuits.

PHOTORESIST APPLICATIONS

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The photopolymerizable compositions may contain other components such as thermal polymerization inhibitors, dyes and pigments, optical brighteners and the like to stabilize, color or otherwise enhance the composition.

Thermal polymerization inhibitors that can be used in the photopolymerizable compositions are: p-methoxyphenol, hydroquinone, and alkyl and aryl-substituted hydroquinones and quinones, tert-butyl catechol, pyrogallol, copper resinate, naphthylamines, diethyl hydroxyl amine, beta-naphthol, cuprous chloride, 2,6-di-tert-butyl-p-creosol, phenothiazine, pyridine, nitrobenzene and dinitrobenzene, p-tolidquinone and chloranil. Also useful for thermal polymerization inhibitors are the nitroso compositions disclosed in U.S. 4,168,982.

Various dyes and pigments may be added to increase the visibility of the resist image. Any colorant used, however, should preferably be translatable to the clinic radiation used.

Useful optical brighteners include those disclosed in Held U.S. Patent 3,854,950. A preferred optical brightener is 7-(4-chloro-6-diethylamino-1,3,5-triazine-4-yl) amino-3-phenyl coumarin. Ultraviolet radiation absorbing materials useful in the invention are also disclosed in Held U.S. Patent 3,854,950.

OTHER COMPONENTS

ADHESION PROMOTER

01

atrapurites, and montmorillonites; finely divided powders having a particle size of 50 millimicrons to 50 microns as disclosed in U.S. Patent 3,891,441 such as silicon oxide, titianium oxide, carbon black, zinc oxide, and other commercially available pigments; and the binder-associates, transparent, inorganic particles as disclosed in European Patent Application 8713013.4 such as magnesium silicate (talc), aluminum silicate (clay), calcium carbonate and alumina. Typically, the filter will be transsparent to actinic radiation to preclude adverse effects during imaging exposure. Depending on its function in the photopolymerizable composition, the filter may be colloidal or have an average particle size of 50 microns or more in diameter.

RESIST APPLICATION

including which a thermosetting polymer or a polymer of a vinyl monomer, a methacrylic acid; MMA is methyl methacrylate; HEMA is 2-hydroxyethyl methacrylate; BMA is butyl methacrylate; EGDMA is ethylene glycol dimethacrylate; BA is butyl acrylate; MMA is isobutyl acrylate; and S is styrene.

The photopolymerizable composition typically contains a thermally activated crosslinking component and a photoinitiator, which release radicals or the chain transfer agent after step (c) the rest areas typically are cured by heating, by uniformly exposing to actinic radiation, by

(3) An imaging system activated by electron radiation
(b) Image-wise exposing the layer to form exposed and unexposed areas,
(c) removing unexposed areas of the layer to form a stencil solder mask image in the exposed areas and

(3) an inhibiting system activated by actinic radiation; groups; and

(2) an addition polymerizable monomer containing at least two terminal, ethylenically unsaturated polymeric hydrocarbon radicals.

(ii) the two polymer networks are formed simultaneously, simultaneously, or sequentially; (iii) independent and non-interfering mechanisms of polymerization, and wherein at least one of the polymer networks contains at least 0.5% by weight of branch or graft linear polymer segments;

(i) the two polymer networks are formed sequentially wherein the second polymer is formed in a solvent dispersion of the first formed polymer network, or

crosslinked in the immobile phase of the chain, and the solvent that provides at least one of the polymer networks is formed by polymerization in a solvent and that does of the following takes place in formation of two polymer networks:

(1) a composition of matter comprising at least two polymer networks which are polymerized and/or crosslinked in the immediate presence of one another, and are dispersible in a solvent with the

such secondary bonding on the surface of the substrate, which is necessary for the formation of a composite.

to form a multilayer printed circuit board.

layer. The entire surface of the first circuit layer is then catalyzed and the process is repeated one or more times.

soldered in place to form the package electrical components. In this manner much time and effort

circuit board having a cured solder mask layer covering all areas except all areas for through-hole areas.

5 developed solder mask image may first be treated to further cure or harden it by baking at elevated temperatures, by additional uniform exposure to actinic radiation or a combination thereof to produce a

directionally. In the second instance, the hardened resist is first stripped from the unpatterned copper surfaces which is then etched or removed from the substrate to form a plated printed circuit board.

etc., may be plated thereover. In the first instance, the hardened exposed resist is typically removed from the remaining copper surface by a stripping process to form the circuit board

then modelled by etching or removing material through a combination of developing a resist mask and

otherwise disperses the unexposed areas without adversely affecting the integrity or adhesion of the surface areas. The substrate which were uncovered by the development process are exposed areas. These areas of the substrate are removed by stripping a material therefrom or depositing a material thereon.

primed chariot pattern on the second day of the month. The chariot was then exposed to the sun for a few hours, after which it was placed in a dark room. The next morning, the chariot had completely dissolved, leaving only a thin film of resin on the surface.

Printed circuit substrate which typically is a copper clad fibreglass epoxy board for primary imaging or a printed circuit relief pattern on the board for secondary imaging. The applied photopolymerizable layer is

The resulting solution was heated to reflux temperature and held there, with stirring.

Methyl acrylic acid (MAA)	3.31	7.93	11.89	15.50
Buyl methacrylate (BMA)				
Hydroxymethyl methacrylate (HEMA)				
Methyl ethyl ketone				

55

05

To a clean reaction vessel were added:

Solution (1) to be used in subsequent polymer preparation, is prepared using the macromer

45 Example 1

In instances where a dry film, e.g., solder mask, is to be laminated to a substrate having a low relief like circuit board, measures must be taken to eliminate entrapped air, e.g., from around circuit lines. Extrapped air is eliminated by the vacuum lamination process of Freil U.S. Patent 4,127,436, by the grooved roll lamination process of Collier et al., U.S. Patent 4,071,367, or by using liquid treating agents as described in Fickes supra, Lau et al. supra, O'Neill et al. supra or Sullivan 4,044 supra.

63

A pre-formed, dry-film, photopolymerizable resist layer typically is applied from a multi-ply, transfer, resist element using the lamination process as described in U.S. Patent 3,493,982. The multi-ply, resist element comprises, in order, an acetic acid radiation transparent, removable support film, e.g., polyethylene, a thin photopolymerizable resist layer, and optionally a removable cover sheet, e.g., polyethylene, to protect the resist element during storage. As described in Celeste supra, the cover sheet, if present, is first removed and the uncrosslinked photoresist surface is laminated to the surface of a copperclad printed circuit substrate using heat and/or pressure, e.g., with a conventional hot-roll laminator. Although the laminate is typically imagedwise exposed to actinic radiation through the temporary support film, in some instances, where the photoresist layer is insensitive to ambient constituents, like oxygen, the temporary support may be removed before imaging to improve resolution and other such properties. In some instances, the resist adhesion to the substrate can be improved by treating the substrate surface with a liquid at or just prior to lamination. Typically, the liquid is insensitive to actinic radiation and may be a solution of adhesions resists as disclosed in Jones U.S. Patent 3,645,772, a solvent or swelling agent for the resist layer as disclosed in Fickes U.S. Patent 4,069,076, a non-solvent, as disclosed in Cohen U.S. Patent 4,405,394 and European Patent 0041639, Piletti et al. U.S. Patent 4,378,264, and Werner et al. European Patent 0040842, or a liquid component of the resist layer as disclosed in Lau et al., U.S. Patent 4,698,294. The liquid in some instances may be photoresistive such as the photoresist solutions disclosed in Isaacson et al. U.S. Patent 3,629,036 which is disclosed in U.S. Patent 3,629,036.

03

51

DRY FILM LAMINATION

The photopolymerizable resist may be a dispersion or solution of the printed circuit substrate using conventional coating process. The liquid may be a liquid onto the resist wherein the solvent is removed subsequently to form a dry, solid, resist layer, or the liquid may be a neat, solvent-free, resist which, subsequently to coating, is directly imaged or exposed to actinic radiation to form a hardened resist layer. The liquids may be roller-coated, spin-coated, screen-coated, or printed as disclosed in Goombs et al., U.S. Patent 4,064,287, or in Dodi et al., U.S. Patent 4,376,815. The liquid, typically as a dispersion or solution, may also be coated and imaged using processes as disclosed in Losert et al., U.S. Patent 4,230,793. Neat liquids may be coated and imaged using processes as disclosed in Heierl U.S. Patent 4,548,884, Hause U.S. Patent B1 4,528,261 or Sullivan, U.S. Patents 4,424,089 and 4,591,265.

COATING LIQUIDS

The photopolymerizable resists may be applied to a printed circuit substrate either as a liquid, as a preformed dry film, or as a combination of a liquid and dry film.

- 5 The following solution, previously mixed for 15 minutes under nitrogen, was then rapidly added to the reaction vessel:
- | | | |
|--------|---------------------|--|
| Amount | Methyl ethyl ketone | Vazo® 52 catalyst 2,2'-azobisis(2,4-dimethylpentane nitrite) |
| 1.56 | 0.004 | 0.023 |
- 15 Solution (A)
- 5 The following solutions, previously mixed for 15 minutes under nitrogen, were then simultaneously added to the reaction vessel:
- | | | | |
|--------|---------------------|-------|----------|
| Amount | Methyl ethyl ketone | SCT | Vazo® 52 |
| 8.79 | 0.007 | 0.252 | 0.252 |
- 15 Solution (A)
- 20 Solution (B)
- 25 Solution (A) was fed so that 54.8% was added over a 90-minute period and 45.2% over a 240-minute period; solution (B) was fed so that 67% was added over a 120-minute period and 33% over a 240-minute period. The reaction mass was held at reflux temperature, with stirring, for 45 minutes, and then 6.9 parts of methyl ketone were added. The mass was then held for another 30 minutes, and then 6.9 parts of methyl ketone were added. The mass was held at reflux temperature, with stirring, for 45 minutes, and then 6.9 parts of cooled to 50°C and filtered to give Macromer solution (1).
- 30 Polymer Product (A) of this invention was prepared using the following procedures:
- To a reaction vessel were added:
- 35 Macromer solution (1)
- | | | | | |
|--------|-------------|-----------------------------------|---------------------------------------|---------------------|
| Amount | Styrene (S) | Hydroxymethyl methacrylate (HEMA) | Ethyleneglycol dimethacrylate (EGDMA) | Methyl ethyl ketone |
| 21.79 | 16.41 | 6.55 | 6.55 | 9.91 |
- 40 Macromer solution (BA)
- | | | |
|--------|---------------------|--|
| Amount | Butyl acrylate (BA) | |
| 21.79 | 16.41 | |
- 45 This reaction mass was heated to reflux temperature and held there, with stirring, while there was added, over a 5-minute period, a solution of:
- 50 Vazo® 67 (2,2'-azobisis(2-methylpentane nitrite))
- | | | |
|--------|---------------------|---|
| Amount | Methyl ethyl ketone | Vazo® 67 (2,2'-azobisis(2-methylpentane nitrite)) |
| 2.18 | 1.31 | 1.31 |
- 55 The reaction mass was then held at reflux temperature, with stirring, for 120 minutes.

55

A dry-film, photosensitive solder mask element was prepared as follows:

Example 2

56

This product was formed into pellets by drying it in an extrusion devolatilizer.

57

87.2/12/0.8 MMA/MAA/EGDMA

and the other polymer network is

58

45/30/25 BMAs/HEMA/MAA

37.7/15/15/2/3/30 where Macromer (1) is

59

BAs/HEMA/EGDMA/Macromer (1)

The mass was then held at reflux temperature, with stirring, for 240 minutes, to give a polymer product.

40

Amount	Methyl ethyl ketone	0.146	Vazo@34	0.024
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41

following solution was added:

The reaction mass was again held at reflux temperature for 120 minutes, with stirring, and then the

42

Amount	Methyl ethyl ketone	0.34	Vazo@67	0.17
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43

followed by a solution containing:

44

Amount	Ethyleneglycoldimethacrylate (EGDMA)	0.039	Methacrylic acid	0.582
	Methyl methacrylate	4.23	Methyl ethyl ketone	8.26
		0.87		Vazo@67
		0.34		0.17

45

The following solution was then added:

The reaction mass was then held at reflux temperature, with stirring, for 120 minutes.

46

Amount	Methyl ethyl ketone	0.87	Vazo@67	0.22
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47

The following solution was then added:

The reaction mass was then held at reflux temperature, with stirring, for 120 minutes.

48

Amount	Methyl ethyl ketone	1.31	Vazo@67	0.22
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49

A macroscopic solution (2) was prepared similarly to the preparation of macroscopic solution (1), except that the macroscopic composition was changed from BMA/HEMA/MMA (45/30/25) for Macroomer 1, to BMA/HEMA/MMA (43/2/30/25) for Macroomer 2. A macroscopic solution (2) was prepared similarly to the preparation of macroscopic solution (1), except the polymer composition was changed from BA/HEMA/EGDMA/Macroomer (2) (35/2/1/4/1/8/35) (37/1/5/15/2/30) for the first polymer network to BA/HEMA/EGDMA/Macroomer (2) (35/2/1/4/1/8/35). The composition of the other polymer network remained the same as in Example 1, i.e.,

Example 3

55

The panels were held for 30 minutes after lamination and then given an exposure of 350 millijoules/cm² to ultraviolet light on DuPont's PC-130 exposure unit. After exposure the Mylar® polyethylene terephthalate film was removed and the sample was developed in an ADS processor with a 1% aqueous sodium carbonate solution at 105°F. Development time was about 284 seconds. After development, each side of each board was cured in an Argus UV unit, first for an exposure of 2 joules/cm², then cooling the board, then for an exposure of 6 joules/cm². The boards were then baked for one hour at 150°C. The resulting solder mask permanency adhered to each printed circuit board is a triple interpenetrating polymer network substantially filling the solder mask image.

The boards gave successful results as a solder mask when evaluated in a typical manner for solder mask properties including tests for solder resistance, solvent resistance, electrical properties, adhesion, thermal shock resistance and flammability. Testing followed the standard specification procedure recommended by the Institute for Interconnecting and Packaging Electronic Circuits present in their publication IPC-SM-840.

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The monomer wet panels while held in a vertical position were passed in a horizontal direction through a nip of two rolls while the dry photosensitive layer was laminated onto the wet panels after first removing the polyethylene film therefrom. The temperature of the rolls was about 140° F. with nip pressure of about 35 psi controlled by air cylinders. Each roll was of a type employed in a VALU™ System lamination and contained a Telion® polytetrafluoroethylene sleeve covering a normal rubber coating.

88

The composition was dispersed or dissolved for coating in 9106 parts by weight of solvent comprising 90% methylene chloride and 10% methanol. This solution was then coated on Mylar®92D polyethylene terephthalate film (E.I. du Pont de Nemours and Company) and air-dried at 150°F. To give a dry photoresistive layer 2 mils thick. This layer was top-laminated with matte, 1 mil polyethylene film with the smooth side to the coating, to give a dry-film, photoresistive, solder mask element.

5

0

9

Solder Mask Composition	Amount
Pentaerythritol triacrylate	450.0
Trimethylol propane triacrylate	450.0
Homopolymer of hexamethylene diisocyanate blocked with methyl ethyl ketone (Desmodur®BL-3175A) (75% solids)	817.8
Dibutyl hydroxylamine	1.5
Micellar's Ketone	3.0
3-Mercapto-1H-1,2,4-triazole	6.0
Green colorant (Dayglo® 122-9655)	90.0
Polymer product (A) of Example 1	1264.5
Amphiphilic copolymer formed from 40% N-t-octyl acrylamide, 34% methyl methacrylate, 16% acrylic acid, 6% hydroxypropyl methacrylate and 4% t-butyl aminoethyl methacrylate; mol. wt. ca. 50,000	60.0
PVP K-90 (polyvinyl pyrrolidone)	180.0

The reaction mass was then held at reflux temperature, with stirring, for 120 minutes.

Methyl ethyl ketone	Vazo-67 (2,2'-azobisis(2-3.5 methylpentane nitrite))	7.0	3.5
Amount			

55

50 This reaction mass was heated to reflux temperature and held there, with stirring, while there was added, over a 5-minute period, a solution of:

Acrylic acid (AA)	Styrene (S)	Hydroxyethyl methacrylate (HEMA)	Ethylene glycol dimethacrylate (EGDMA)	Methyl ethyl ketone
15.0	61.7	7.0	1.3	71.5
Butyl acrylate (BA)				
15.0	61.7	7.0	1.3	71.5
Amount				

45

40

To a reaction vessel were added:

Polymer Product (C) of this invention was prepared using the following procedures:

Example 5

35

The boards gave successful results as a solder mask when evaluated in the typical manner for solder mask properties as set forth in Example 2.

The dry-film, photosensitive solder mask was applied to a series of printed circuit board panels, processed and evaluated similarly to that described in Example 2.

The coating, to give a dry-film, photosensitive, solder mask element, layer 2 mils thick. This layer was top-laminated with matte, 1 mil polyethylene film with the smooth side to the coating, to give a dry-film, photosensitive, solder mask element.

Layer 2 mils thick. This layer was air-dried at 150°F to give a dry photosensitive thialate film (E. I. du Pont de Nemours and Company) and then coated on Mylar®92D polyethylene terephthalate film (E. I. du Pont de Nemours and Company) and then coated on Mylar®92D polyethylene terephthalate film.

The composition was dispersed or dissolved for coating at 25% by weight in solvent comprising 92% methylene chloride and 8% methanol. This solution was then coated on Mylar®92D polyethylene terephthalate film.

30

25

20

Solder Mask Composition	Amount	Homopolymer of hexamethylene diisocyanate blocked with methyl ethyl ketoxime (Desmodur®BL-3175A)(75% solids)	168.4	168.4	Penetrating triacrylate	0.53	0.53	Diethyl hydroxylamine	36.8	Ethyl Michler's ketone	1.9	3-mercapto-1H-1,2,4-triazole	1.9	Green colorant (Dayglo® 122-9655)	5.3	477.4	Polymer Product (B) of Example 3	28.9	Amphoteric copolymer formed from 40% N-t-octyl acrylamide, 34%	31.5	methacrylate, 16% acrylic acid, 6% hydroxypropyl methacrylate	31.5	and 4% t-butyl amineethyl methacrylate; mol. wt. ca. 50,000	31.5	PVP K-90 (polyvinyl pyrrolidone)	31.5

15

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5

A dry-film, photosensitive solder mask element was prepared as follows:

Example 4

MMA/MA/EGDMA: (87.2/12/0.8).

55

56

45

Example 6

A dry-film, photosensitive solder mask element was prepared as follows:

40

EMA/MAA/EGDMA

45

and the other polymer network is

50

BA/S/HEMA/EGDMA/AA

55

Polymer Product (C), in which one polymer network is

60

61.7/15.7/1.3/15

65

87.4/12.0.6.

70

This product was used in solution as prepared (55% solids).

Vazo@67	0.10
Methyl ethyl ketone	0.60
Amount	

30

The mass was then held at reflux temperature, with stirring, for 240 minutes, to give a polymer product,

35

following solution was added:

40

The reaction mass was again held at reflux temperature for 120 minutes, with stirring, and then the

45

Vazo@67	0.07
Methyl ethyl ketone	1.4
Amount	

50

followed by a solution containing:

55

Methyl ethyl ketone	14.3
Ethyl methacrylate	17.5
Methacrylic acid	24
Ethylene glycol dimethacrylate (EGDMA)	0.12
Amount	

60

To 148.4 parts of the above solution the following solution was then added:
The reaction mass was then held at reflux temperature, with stirring, for 240 minutes.

65

Vazo@67	0.5
Methyl ethyl ketone	3.0
Amount	

70

The following solution was then added to the reaction mass:

75

55 This was charged to a reaction vessel, heated to reflux temperature and held there. To it was then added, with stirring over a 45 minute period, a mixture of

50	Product of (1)	738.51 parts	Ethyl acetate	Dibutyltin dilaurate	0.90
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(2) A mixture was prepared of the mixture was allowed to rise to about 260°C. When the temperature of the effluent vapor dropped to about 90°C and the acid number was about 3, the reaction was stopped; and the temperature of the mixture was held there, with stirring. Water removal was then begun

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This mixture was heated to 155-165°C and held there, with stirring. Water removal was then begun

40	Neopenetyl glycol	1439.25 parts	Isooctylidic acid	Dodecanedioic acid	612.05
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(1) To a reaction vessel were charged:
Sequential Preparation of a PEU-Acrylic Catenated System:

35

Example 7

30 mask properties as set forth in Example 2.
The boards gave successful results as a solder mask when evaluated in the typical manner for solder temperature of each board panel existing the vacuum laminator was about 150°F.
conventionally vacuum laminated with the dry-film, photosensitive solder mask element, so that the both panel surfaces with approximately 200 holes ranging in size from 35 mils diameter to 3.5 mils containing a raised relief height of about 3.5 mils
A series of printed circuit board panels of a size 6"x6" were coated on Mylar® 92D ball milled in solvent first before adding the other ingredients. (The filter and Polymer Product (C) were methylene chloride and 8% methanol, and ball milled overnight. The solution was then coated on Mylar® 92D ball milled in solvent first before adding the other ingredients. (The filter and Polymer Product (C) were

30

The composition was dispersed or dissolved for coating at 35% by weight in solvent comprising 92%

25

5	Solder Mask Composition	Amount
10	Pentaerythritol triacrylate	12.8
15	Triethylol propane triacrylate	12.8
20	Benzophenone	0.04
25	Diethyl hydroxylamine	3.4
30	Ethyl Michler's ketone	0.03
35	3-mercaptop-1-H-1,2,4-triazole	0.17
40	Green colorant (HVT-45)	2.6
45	Polymer Product (C) of Example 5 (55% solids)	67.1
50	Cyprubond® talc filter	1.5
55	Amphoteric copolymer formed from 40% N-t-octyl acrylamide, 34%	15.0
60	methacrylate, 16% acrylic acid, 6% hydroxypropyl methacrylate and 4% t-butyl aminoethyl methacrylate; mol. wt. ca. 50,000.	1.7
65	PVP-K-90 (polyvinyl pyrrolidone)	2.6

To a reaction vessel were charged

Butanol	350.00 parts	Ethyleneglycol monobutyl ether	350.00 parts
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55

This mixture was heated to 150-160°C, under nitrogen, with stirring. Water removal was then begun and the temperature of the mixture was allowed to rise to 260-270°C. This temperature was maintained until the reaction mixture had an acid number of 1 or less. The mixture was then cooled and to it was added a mixture of

Trimethylol propane	363.42 parts	Ethyleneglycol	840.44
Terephthalic acid	449.94	Isophthalic acid	674.84
Adipic acid	840.98	Maleic anhydride	99.52

45

40

(1) To a reaction vessel were charged

Concurrent Preparation of an Epox/S/EA/MASS/Unsaturated PE Catenated System:

Example 8

35

The resulting dispersion was stable after eight months of storage. A film of the dispersion drawn on a glass plate was smooth, glossy and transparent. The dispersion was held for four hours at reflux temperature, with stirring, 84.8 parts of a 1/1 mixture of aromatic hydrocarbon (Solvesso 100) and dimethyl esters of mixed C₉-C₁₂ dibasic acids were added, and the mixture cooled.

This was held for four hours at reflux temperature, with stirring, 84.8 parts of a 1/1 mixture of aromatic hydrocarbon (Solvesso 100) and dimethyl esters of mixed C₉-C₁₂ dibasic acids were added, and the mixture cooled.

Vazo@67	0.57 parts	Methyl ethyl ketone	3.41
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25

The resulting mixture was held at reflux for 2 hours, and to it was then added a mixture of

Vazo@67 [2,2'-azobis-(2-methylbutyronitrile)]	4.05 parts	Methyl ethyl ketone	7.93
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20

This mixture was heated to reflux temperature and held there with stirring. To it was then added a mixture of

Methyl methacrylate	59.8 parts	Styrene	23.15
Glycidyl methacrylate	11.58	Buyl methacrylate	1.39
1,6-hexanediol diacrylate	82.96	Methyl ethyl ketone	1.39

15

10

(3) To a reaction vessel were added 365.62 parts of (2) and a mixture of

Desmodur@ W (difunctional isocyanate)	144.02 parts	Desmodur@ N (trifunctional isocyanate, 75% solids in ethyl acetate)	41.177
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5

(1) A mixture was prepared of

Sequential Preparation of a S/B/A/HEMA/EDMA/EGDMA/HEMA/EGDMA Catenated System:

Example 9

glasses plate was glossy and smooth, with a blue-white transparent haze.

The mixture was then cooled and brought to a solids content of 25% with Cellulosolve acetate. The resulting transparent dispersion was stable after 3 years of storage. A film of the dispersion drawn on a

two hour intervals.

The reaction mixture was then held at reflux while two additional portions of solution (a) were added at

Trimethylbenzyl ammonium hydroxide (40% solids in methanol)	0.19 parts	4.32	2.88 parts	3.16
(a) Di-t-butyl peroxide			Cellulosolve acetate	

The mixture was heated to reflux, with stirring, and to it was added a solution of

Silrene	363.43 parts	11.51	Epon 1004 (65% solids in methyl ethyl ketone)
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To this was added, with stirring a mixture of

Product of (1)	23.98 parts	133.97	157.42	9.40
Product of (2)			Cellulosolve acetate	Methyl ethyl ketone

(3) To a reaction vessel were charged

hours and cooled.

Butanol, 58.6 parts, was added to the mixture, which was then held at reflux temperature for two

Styrene	303.0	839.0	154.4	177.7
Methacrylic acid				
Ethyl acrylate	662.5 parts			
t-Buyl perbenzoate				

then added, over a 2-hour period, a mixture of

This mixture was heated to reflux temperature, under nitrogen, and held there with stirring. To it was

Butyl Cellulosolve acetate	685.5 parts	243.6	174.5	0.2
Butanol				
Ethyl acetate				

55

To a reaction vessel were charged
Sequential Preparation of a PEU Network-PVP Network Catenated System:

Example 10

45

dispersion drawn on a glass plate was transparent and glossy, with a slight blue haze.
The resulting reddish dispersion was transparent and stable after storage for two months. A film of the
This reaction mixture was then held at reflux temperature for two hours and cooled.

Vazo@67	57.7 parts	Isopropenol	129.0	Methyl ethyl ketone	70.0
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40

This was then heated at reflux temperature, under nitrogen, with stirring, for two hours. To it was then
added a mixture of

Vazo@67	57.7 parts	Isopropenol	129.0	Methyl ethyl ketone	70.0
---------	------------	-------------	-------	---------------------	------

35

This mixture was heated to reflux temperature, held there for five minutes, and to it was added, over a
5-minute period, a mixture of

Product of (1)	1500.0 parts	4-vinylpyridine	169.0	Hydroxymethyl methacrylate	19.2
				Ethylene glycol dimethacrylate	5.0

30

(2) A reaction vessel was charged with
The mixture was then heated at reflux temperature for two hours and then cooled.

25

Vazo@67	8.1 parts	Methyl ethyl ketone	54.0	Vazo@67	8.1 parts
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20

This mixture was heated at reflux temperature, with stirring, for two hours. To it was then added a
solution of

Vazo@67	56.7 parts	Isopropenol	129.0	Methyl ethyl ketone	70.0
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15

This mixture was charged to a reaction vessel, heated to reflux temperature and held there, and to it
was then added, over a 5-minute period, a mixture of

Styrene	450.0 parts	Diethylaminooethyl methylacrylate	75.0	Butyl acrylate	723.0
		Hydroxymethyl methacrylate	225.0	Ethylene glycol dimethacrylate	27.0
			252.2	Isopropenol	1252.2

10

(B) To a reaction vessel were charged
50 The mixture was then held at reflux temperature with stirring for four hours, and then cooled.

Vazo@67	4.85 parts	Methyl ethyl ketone	29.12
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The reaction mixture was held at reflux temperature, with stirring, for two hours. To it was then added
a mixture of

Vazo@67	33.97 parts	Methyl ethyl ketone	67.94
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This mixture was heated to reflux temperature, under nitrogen, with stirring, and to it was added, over
a five-minute period, a mixture of

Buyl acrylate	710.49 parts	Syrene	145.59
Hydroxyethyl methacrylate	97.06	Ethylene glycol dimethacrylate	17.47
Methyl ethyl ketone	693.50	Ethylene glycol diacrylate	17.47

(A) To a reaction vessel were charged
30 Sequential Preparation of a S/B/A/EGDMA/HEMA/EGDMA/HEMA Catenated System:

Example 11

The resulting transparent dispersion was stable after 6 months of storage. A film of the dispersion drawn
on glass was transparent and glossy.
20 mixture of aromatic hydrocarbon (Solvesso 100) and dimethyl esters of mixed C_9-C_{12} dibasic acids.
Refluxing of the mixture was continued for four hours, and to it was then added 94.6 parts of a 1/1

Vazo@67	0.18 parts	Methyl ethyl ketone	1.06
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The mixture was then held at reflux temperature for two hours, and to it was added a mixture of

Vazo@67	1.24 parts	Methyl ethyl ketone	2.47
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This mixture was heated at reflux temperature, under nitrogen, for five minutes. To it was then added,
over a five-minute period, a mixture of

Polyesteretherthane resin prepared as in Example 7(2)	265.22 parts	1-Vinyl-2-pyrrolidone	29.84
1,6-Hexamethylene diacrylate	0.40		

Example 13

55 This mixture was heated to reflux temperature, under nitrogen, with stirring, and held there for 5 hours. It was then cooled. The resulting homogeneous translucent dispersion was stable after four months of storage. A film of the dispersion drawn on glass was uniform and glossy.

Product of (A)	120.54 parts	31.08	Methyl methacrylate
		3.50	Hydroxyethyl methacrylate
		0.42	Ethylene glycol dimethacrylate
		25.00	Methyl ethyl ketone
Vazo@67	1.23 parts	0.18 parts	Methyl ethyl ketone
Vazo@67	1.05	1.05	Methyl ethyl ketone

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1. A composition of matter comprising at least two polymer networks which
 (a) are polymerized and/or crosslinked in the immediate presence of one another, and
 (b) are dispersible in a solvent with the proviso that at least one of the polymer networks is formed
 by polymerization in a solvent and that one of the following takes place in formation of two polymer
 networks:
 (i) the two polymer networks are formed sequentially wherein the second polymer network is
 formed in a solvent dispersion of the first formed polymer network,
 (ii) the two polymer networks are formed simultaneously or substantially simultaneously by
 independent and non-interfering mechanisms of polymerization.
2. The composition of claim 1 wherein the two polymer networks are formed in the substantial absence of
 phase separation in a common portion of the two polymer networks.
3. The composition of claim 2 wherein one of the two polymer networks has a first segment which exists in a common portion of the two polymer networks and a second segment which exists solely in a portion of the
 one polymer network which is separate and distinct from the other polymer network.
4. The composition of claim 1 wherein the solvent is an organic solvent.
5. The composition of claim 1 wherein in (b) the two polymer networks are dispersible in a solvent.
6. The composition of claim 5 wherein the solvent is a solvent for a precursor which forms a substantial
 portion of a polymer network.
7. The composition of claim 1 wherein each polymer network has a gel point and wherein polymerization
 of at least one polymer network is terminated before, substantially at, or near the gel point of the
 polymer network.

Claims

30 1. A composition of matter comprising at least two polymer networks which
 (a) are polymerized and/or crosslinked in the immediate presence of one another, and
 (b) are dispersible in a solvent with the proviso that at least one of the polymer networks is formed
 by polymerization in a solvent and that one of the following takes place in formation of two polymer
 networks:
 (i) the two polymer networks are formed sequentially wherein the second polymer network is
 formed in a solvent dispersion of the first formed polymer network,
 (ii) the two polymer networks are formed simultaneously or substantially simultaneously by
 independent and non-interfering mechanisms of polymerization.

2. The resulting translucent dispersion was stable after a storage period of three months. A film of the
 mixture of aromatic hydrocarbon (Solvesso 100) and dimethyl esters of mixed C9-C12 dibasic acids.
 Refluxing of the mixture was continued for four hours, and to it was then added 94.6 parts of a 1/1
 mixture of aromatic hydrocarbon (Solvesso 100) and dimethyl esters of mixed C9-C12 dibasic acids.

Vazo® 67	1.24 parts	Methyl ethyl ketone	2.47
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35 This mixture was heated at reflux temperature, under nitrogen, for five minutes. To it was then added,
 over a five-minute period, a mixture of
 Vazo® 67

Vazo® 67	0.18 parts	Methyl ethyl ketone	1.06
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40 This mixture was heated at reflux temperature, under nitrogen, for five minutes. To it was then added,
 over a five-minute period, a mixture of
 Vazo® 67

Polyesteretherane resin prepared as in Example 7(2)	265.22 parts	Vinyl acetate	29.84
		1,6-hexamethylene diacrylate	0.40

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To a reaction vessel were charged
 Sequential Preparation of a PEU Network-PVAc Network Catenated System

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|-----|--|
| 36. | The composition of claim 33 wherein the polymer networks contain at least 0.5% by weight of branch or graft linear polymer segments. |
| 35. | The composition of claim 34 wherein the remaining polymer component(s) is a polymer network, and wherein the polymer components cannot be totally physically separated from one another. |
| 34. | The composition of claim 33 wherein the remaining polymer component(s) is a linear or branched polymer, a solvent dispersible polymer or a polymer network not capable of being swollen dispersed or dissolved. |
| 33. | A composition of matter comprising at least three polymer components wherein at least two of the polymer components are polymer networks which are polymerized and/or crosslinked in the immediate presence of one another, and wherein the two polymer networks are formed sequentially where the second polymer network is formed in a solvent solution or dispersion of the first formed polymer network, or in a solvent dispersible polymer which are formed sequentially where the second polymer network is formed in the immediate presence of the first formed polymer network, and the two polymer networks are formed simultaneously by independent and non-interacting mechanisms of polymerization; |
| 32. | A composition of matter comprising a polymer network and a linear or branched polymer which are dispersible or dissolvable in a solvent and that one of the following takes place in formation of the polymer network: (i) the polymer network is formed in a solvent solution or dispersion of the linear or branched polymer; (ii) the polymer network is formed in a solvent solution or dispersion of the branched polymer; (iii) the polymer network is formed in a solvent solution or dispersion of the linear or branched polymer, or either order, the polymer network (or linear or branched polymer) is formed in a solvent solution or dispersion of the linear or branched polymer; |
| 31. | The composition of claim 30 wherein the macromer is a linear polymer precursor having a terminal polymethylizable ethylenic group. |
| 30. | The composition of claim 29 wherein the branch or graft linear polymer segments are formed during formation of the polymer network from at least one macromer. |
| 29. | A composition of matter comprising a polymer network containing at least 0.5%, by weight of branch or graft linear polymer segments, wherein the polymer network is dispersible in a solvent and wherein the graft linear polymer segments, wherein the polymer network is formed by polymerization in a solvent. |
| 28. | The composition of claim 24 wherein the linear polymer segment has a weight average molecular weight between about 250 and about 10,000. |
| 27. | The composition of claim 24 wherein the linear polymer segment contains between 2 and 1000 monomeric units. |
| 26. | The composition of claim 25 wherein the macromer is a linear polymer precursor having a terminal polymethylizable ethylenic group. |
| 25. | The composition of claim 24 wherein the linear polymer segment is formed during the formation of the polymer network from at least one macromer. |
| 24. | (c) wherein at least one of the polymer networks contains at least 0.5% by weight of branch or graft linear polymer segments. |
| 23. | The composition of claim 24 wherein the linear polymer segment contains between 2 and 1000 monomeric units. |
| 22. | The composition of claim 24 wherein the linear polymer segment has a weight average molecular weight between about 250 and about 10,000. |
| 21. | The composition of claim 24 wherein the linear polymer segment has a weight average molecular weight between about 250 and about 10,000. |
| 20. | The composition of claim 29 wherein the branch or graft linear polymer segments are formed during formation of the polymer network from at least one macromer. |
| 19. | The composition of claim 24 wherein the linear polymer segment has a weight average molecular weight between about 250 and about 10,000. |
| 18. | The composition of claim 24 wherein the linear polymer segment has a weight average molecular weight between about 250 and about 10,000. |
| 17. | The composition of claim 24 wherein the linear polymer segment has a weight average molecular weight between about 250 and about 10,000. |
| 16. | The composition of claim 24 wherein the linear polymer segment has a weight average molecular weight between about 250 and about 10,000. |
| 15. | The composition of claim 24 wherein the linear polymer segment has a weight average molecular weight between about 250 and about 10,000. |
| 14. | The composition of claim 24 wherein the linear polymer segment has a weight average molecular weight between about 250 and about 10,000. |
| 13. | The composition of claim 24 wherein the linear polymer segment has a weight average molecular weight between about 250 and about 10,000. |
| 12. | The composition of claim 24 wherein the linear polymer segment has a weight average molecular weight between about 250 and about 10,000. |
| 11. | The composition of claim 24 wherein the linear polymer segment has a weight average molecular weight between about 250 and about 10,000. |
| 10. | The composition of claim 24 wherein the linear polymer segment contains between 2 and 1000 monomeric units. |
| 9. | The composition of claim 24 wherein the linear polymer segment has a weight average molecular weight between about 250 and about 10,000. |
| 8. | The composition of claim 24 wherein the linear polymer segment has a weight average molecular weight between about 250 and about 10,000. |
| 7. | The composition of claim 24 wherein the linear polymer segment has a weight average molecular weight between about 250 and about 10,000. |
| 6. | The composition of claim 24 wherein the linear polymer segment has a weight average molecular weight between about 250 and about 10,000. |
| 5. | The composition of claim 24 wherein the linear polymer segment has a weight average molecular weight between about 250 and about 10,000. |
| 4. | The composition of claim 24 wherein the linear polymer segment has a weight average molecular weight between about 250 and about 10,000. |
| 3. | The composition of claim 24 wherein the linear polymer segment has a weight average molecular weight between about 250 and about 10,000. |
| 2. | The composition of claim 24 wherein the linear polymer segment has a weight average molecular weight between about 250 and about 10,000. |
| 1. | The composition of claim 24 wherein the linear polymer segment has a weight average molecular weight between about 250 and about 10,000. |

45. The composition of claim 44 wherein the linear polymer segments are vinyl or acrylic polymers or branched polymers are acrylic, epoxy or urethane polymers or combinations thereof.

44. The composition of claim 1 wherein the polymer networks, linear polymer segments or linear or amino, amide, vinyl or urethane, isocyanate, blocked isocyanate groups or combinations thereof.

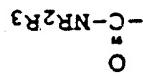
43. The composition of claim 40 wherein the linear polymer segments bear one or more carboxy, hydroxy, isocyanate groups or combinations thereof.

42. The composition of claim 40 wherein at least one of the polymer networks or linear or branched polymers bears one or more carboxy, hydroxy, amino, amide, vinyl, urethane, isocyanate, blocked combinations thereof.

41. The composition of claim 40 wherein the functional group is a carboxy, a hydroxy, an amino group, a vinyl group, a urethane group, an isocyanate group, a blocked isocyanate group or amide group, a vinyl salt of any of the foregoing.

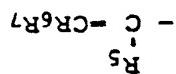
40. R₁₂, R₁₃ and R₁₄ can be hydrogen, alkyl or cycloalkyl of 1-18 carbon atoms, aryl, alkaryl or aralkyl; or OSO₃R₁₂, -OP02R₁₂, -PO2R₁₂, -PR₁₂R₁₃, -PR₁₂R₁₃, -SR₁₂R₁₃, or -N(R₁₂R₁₃R₁₄) where atoms or -OR₁₁ is alkyl or cycloalkyl of 1-18 carbon atoms, aryl, alkaryl or aralkyl; or an acetylacetoxy group; -S(R₉R₁₀) (where R₉, R₁₀ can be alkyl or cycloalkyl of 1-18 carbon atoms or urethane group; a quinone diimide group; an azo group; an azide group; a diazonium group; an azididine group; an isocyanate or blocked isocyanate group; a urea group; an oxirane group; an urethane group; a salt or anilinium salt of any of the foregoing).

35. -COOR or when taken together R₅, R₆ and/or R₇ can form a cyclic or heterocyclic group; -SO₃H;



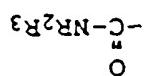
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(where R₅, R₆ and R₇ can be hydrogen, alkyl or cycloalkyl of 1-18 carbon atoms, aryl, alkaryl, aralkyl,



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20. together R₂ and R₃ can form a heterocyclic ring); -CH₂OR₄ (where R₄ is hydrogen, alkyl or cycloalkyl of 1-18 carbon atoms, aryl, alkaryl, aralkyl, or where R₂ and R₃ can be hydrogen, alkyl or cycloalkyl of 1-18 carbon atoms, aryl, alkaryl, aralkyl,



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40. The composition of claim 1 wherein at least one of the polymer networks, linear polymer segments or linear or branched polymers bears one or more functional groups wherein the functional group is -COOR, -OR, -SR (where R can be hydrogen, alkyl or cycloalkyl of 1-18 carbon atoms, aryl, alkaryl or aralkyl, a heterocyclic, or -OR₁, where R₁ can be alkyl of 1-18 carbon atoms, aryl, alkaryl or aralkyl, a halogen; -NR₂R₃ or -CN; halogen; -NR₂R₃ or

39. The composition of claim 24 wherein at least one solvent dispersible polymer network is a sol, a critical gel or a combination thereof.

38. The composition of claim 24 wherein each polymer network has a gel point and wherein polymerization of at least one polymer network is terminated before, substantially all, or near the gel point of the polymer network.

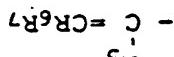
37. The composition of claim 36 wherein the branch linear polymer segments are formed during the formation of the polymer component from at least one macromer.

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(where R_5 , R_6 and R_7 can be hydrogen, alkyl or cycloalkyl of 1-18 carbon atoms, aryl, alkaryl, aralkyl,

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NR₂R₃ (where R_2 and R_3 can be hydrogen, alkyl or cycloalkyl of 1-18 carbon atoms, aryl, alkaryl, aralkyl, -CH₂OR₄ (where R_4 is hydrogen, alkyl or cycloalkyl of 1-18 carbon atoms, aryl, alkaryl, aralkyl), or together R_2 and R_3 can form a heterocyclic ring);

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linear or branched polymers bears one or more functional group wherein the functional group is linear or branched polymer networks, linear polymer segments or COOR, -OR, -SR (where R can be hydrogen, alkyl or cycloalkyl of 1-18 carbon atoms, aryl, alkaryl or aralkyl, a heterocyclic, or -OR₁ where R_1 can be alkyl of 1-18 carbon atoms, aryl, alkaryl or aralkyl); or COO₂R₁₂, -OP₂R₁₂, -PR₁₂R₁₃R₁₄, -OP₂R₁₂, -SR₁₂R₁₃, or -N(R₁₂R₁₃)R₁₄ group (where CN; halogen; NR₂R₃ or

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47. The composition of claim 29 wherein at least one of the polymer networks, linear polymer segments or COOR or when taken together R_5 , R_6 and/or R_7 can form a cyclic or heterocyclic group; -SO₃H; a salt or quinone salt of any of the foregoing; R_{12} , R_{13} and R_{14} can be hydrogen, alkyl or cycloalkyl of 1-18 carbon atoms, aryl, alkaryl or aralkyl); or OSO₃R₁₂, -OP₂R₁₂, -PR₁₂R₁₃R₁₄, -SR₁₂R₁₃, or -N(R₁₂R₁₃)R₁₄ group (where atoms or -OR₁, where R_1 is alkyl or cycloalkyl of 1-18 carbon atoms, aryl, alkaryl or aralkyl); or an acetylacetoxy group; -SIR₈R₉R₁₀ (where R_8 , R_9 and R_{10} can be alkyl or cycloalkyl of 1-18 carbon aziridine group; a quinone diazide group; an azo group; an azide group; a diazonium group; an urethane group; an isocyanate or blocked isocyanate group; a urea group; an oxirane group; an etherane group; a salt or quinone salt of any of the foregoing.

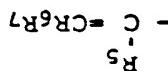
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(where R_5 , R_6 and R_7 can be hydrogen, alkyl or cycloalkyl of 1-18 carbon atoms, aryl, alkaryl, aralkyl,

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together R_2 and R_3 can form a heterocyclic ring); -CH₂OR₄ (where R_4 is hydrogen, alkyl or cycloalkyl of 1-18 carbon atoms, aryl, alkaryl, aralkyl), or -CH₂OR₄ (where R_4 is hydrogen, alkyl or cycloalkyl of 1-18 carbon atoms, aryl, alkaryl, aralkyl, or alkyl, a heterocyclic, or -OR₁ where R_1 can be alkyl of 1-18 carbon atoms, aryl, alkaryl or aralkyl);

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46. The composition of claim 24 wherein at least one of the polymer networks, linear polymer segments or linear or branched polymers bears one or more functional group wherein the functional group is linear or branched polymer networks, linear polymer segments, aryl, alkaryl, aralkyl, alkyl, a heterocyclic, or -OR₁ where R_1 can be hydrogen, alkyl or cycloalkyl of 1-18 carbon atoms, aryl, alkaryl or aralkyl, a heterocyclic, or -OR₁ where R_1 can be alkyl of 1-18 carbon atoms, aryl, alkaryl or aralkyl); or CN; halogen; NR₂R₃ or

combinations thereof.

- 55 (1) a composition of matter comprising at least two polymer networks which are polymerized and/or crosslinked in the immediate presence of one another, and are dispersible in a solvent with that one of the following takes place in formation of two polymer networks:
- 55 (a) applying to a substrate, a photosensitive composition to form the photosensitive layer thereon, the photosensitive composition comprising:
80. A process for imaging a photosensitive layer on a substrate comprising the steps of:
- 50 79. The composition of claim 59 further comprising at least one thermally activated curing agent.
78. The composition of claim 59 having dispersed therein a colorant.
- 45 77. The composition of claim 59 further comprising a linear or branched polymer, an inorganic particulate material or combinations thereof.
76. The composition of claim 74 in which the polymerizable monomer is at least one vinyl or acrylic compound or combinations thereof.
- 40 75. The composition of claim 74 in which the polymerizable monomer contains one or more ethylenically unsaturated groups.
- 35 74. The composition of claim 59 in which component (b) comprises:
73. The composition of claim 59 in which component (b) is bonded to component (a).
- 30 72. The composition of claim 59 in which component (b) is photoconductive or photoinductive.
71. The composition of claim 59 in which component (b) is photomagnetic or a photodemagnetic.
- 25 70. The composition of claim 59 in which component (b) is a material which causes changes in refractive index upon exposure to actinic radiation.
69. The composition of claim 59 in which component (b) is a phototackifier or a photodetackifier.
- 20 68. The composition of claim 59 in which component (b) is photoabsorbable.
67. The composition of claim 59 in which component (b) is photoreducible or photooxidizable.
66. The composition of claim 59 in which component (b) is photochromic.
- 15 65. The composition of claim 59 in which component (b) is photodegradable component.
64. The composition of claim 59 in which component (b) is a photoinhibitor.
63. The composition of claim 59 in which component (b) is a photodesensitizer.
- 10 62. The composition of claim 59 in which component (b) is a photosolubilizer.
61. The composition of claim 59 in which component (b) is a photoinitiator, a photosensitizer or a combination thereof.
- 5 60. The composition of claim 59 in which component (b) generates a free radical, generates an ionic or neutral species or dissociates on exposure to actinic radiation.
- (b) at least one photoactive or thermally active component.

96. A process for forming a solder mask on a printed circuit substrate bearing on its surface, a raised,

(b) an initiating system activated by actinic radiation.

(a) an addition polymerizable ethylenically unsaturated monomer, and

95. The process of claim 80 in which the photoactive component comprises

form a multilayered image.

94. The process of claim 80 wherein after step (c), steps (a), (b) and (c) are repeated one or more times to

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unexposed areas to form a visible surface image.

93. The process of claim 80 wherein colorant or powdered material is adhered to the exposed or

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complimentary unexposed or exposed areas adhered to the substrate.

92. The process of claim 84 wherein the exposed or unexposed areas of the layer are peeled from the

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organic solvent developer therefore.

91. The process of claim 84 wherein the exposed or unexposed areas of the layer are removed with an

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alkaline, aqueous developer therefore.

89. The process of claim 85 wherein after step (c) the resist areas are cured by heating, by uniformly exposing to actinic radiation, by treating with a chemical reagent or by a combination thereof.

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88. The process of claim 86 in which unprotected, substrate, surface areas are modified by depositing a metal thereon by plating or soldering.

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87. The process of claim 86 in which after the substrate surfaces are modified, the resist areas are removed from the substrate.

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86. The process of claim 85 in which after step (c), the unprotected substrate surface areas are permanently modified by etching the substrate surfaces or depositing a material thereon.

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85. The process of claim 84 in which all of the exposed or unexposed areas of the layer are removed from the substrate surface in step (c) to form stencil resist areas and complimentary, unprotected, substrate,

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84. The process of claim 80 in which at least a portion of the exposed or unexposed areas of the layer are removed in step (c) to form a relief image.

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83. The process of claim 80 in which the photosensitive composition is applied by laminating a supported solid photosensitive layer thereon.

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82. The process of claim 80 in which the photosensitive composition is applied as a coating dispersion or photosensitive liquid.

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81. The process of claim 80 in which the photosensitive composition is applied as a neat, solvent-free, with a reactant to develop an image in the exposed or unexposed areas to form an imaged layer.

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(c) modifying exposed or unexposed areas of the layer by removing exposing exposed or unexposed areas, (b) imagewise exposing the layer to actinic radiation to form exposed and unexposed areas,

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(2) at least one photoactive component;

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(ii) the two polymer networks are formed simultaneously or substantially simultaneously by formed in a solvent dispersion of the first formed polymer network, or

(i) the two polymer networks are formed sequentially wherein the second polymer network is

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98. The process of claim 96 wherein the photopolymerizable composition contains a thermally activated crosslinking component.
97. The process of claim 96 wherein after step (c) the resist areas are cured by heating, by uniformly exposing to actinic radiation, by treating with a chemical reagent or by a combination thereof.
- (2) an addition polymerizable monomer containing at least two terminal, ethylenically unsaturated groups; and
- (3) an initiating system activated by actinic radiation;
- (i) the two polymer networks are formed sequentially or substantially simultaneously by independent and non-interfering mechanisms of polymerization, and
- (ii) the two polymer networks place in formation of two polymer networks:
- wherein at least one of the polymer networks contains at least 0.5% by weight of branch or graft linear polymer segments;
- (c) removing unexposed areas of the layer to form a stencil solder mask image in the exposed areas and complementary, unprotected areas of the circuit pattern.
98. The process of claim 96 wherein the photopolymerizable composition contains a thermally activated crosslinking component.

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